Environmental Science & Technology

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Modeling the Contribution of Crops to Nitrogen Pollution in the Yangtze River

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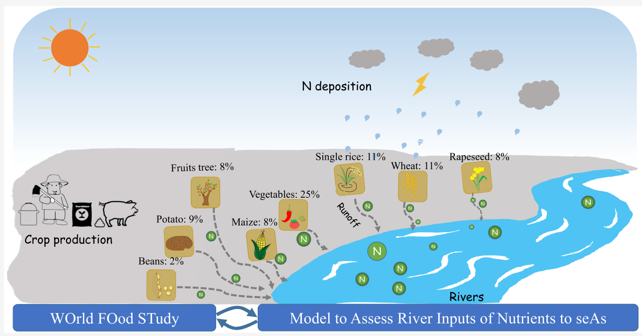
Cite This: *Environ. Sci. Technol.* 2020, 54, 11929−11939 Read Online

ABSTRACT: Agriculture contributes considerably to nitrogen (N) inputs to the world's rivers. In this study, we aim to improve our understanding of the contribution of different crops to N inputs to rivers. To this end, we developed a new model system by linking the MARINA 2.0 (Model to Assess River Input of Nutrient to seAs) and WOFOST (WOrld FOod STudy) models. We applied this linked model system to the Yangtze as an illustrative example. The N inputs to crops in the Yangtze River basin showed large spatial variability. Our results indicate that approximately 6,000 Gg of N entered all rivers of the Yangtze basin from crop production as dissolved inorganic N (DIN) in 2012. Half of this amount is from the production of single rice, wheat, and vegetables, where synthetic fertilizers were largely applied. In general, animal manure contributes 12% to total DIN inputs to rivers. Three-quarters of manure-related DIN in rivers are from vegetable, fruit, and potato production. The contributions of crops to river pollution differ among sub-basins. For example, potato is an important source of DIN in rivers of some upstream sub-basins. Our results may help to prioritize the dominant crop sources for management to mitigate N pollution in the future.



1. INTRODUCTION

Producing enough crop grain to feed an increasing population is one of the societal challenges.[1] Nitrogen (N) is one of the essential elements for producing crops. Since the early 20th century, the invention of the Haber−Bosch process has greatly enhanced the availability of crop production per unit land.[2] However, in high-income and some rapidly developing countries, the increase in crop productivity is generally accompanied by the consumption of synthetic N fertilizers.[3] China is a typical example of this situation. In recent decades, this abundant use of N fertilizers contributed largely to food security in China.[4] Chinese grain production has increased from 132 Mt in 1950 to 607 Mt in 2014 but without expansion of the total planting area.[5] However, the consumption of synthetic N fertilizer in China increased from 1 to 53 Mt over the past 50 years, now accounting for approximately 32% of global consumption.[6] The N surplus in soils from crop production generated enormous environmental concerns and posed substantial risks to air,[7] soil,[8] and water quality[5] in China.

As a result of intensified crop production, water systems in China became polluted.[5,9,10] The Yangtze River basin, an important food-producing area in China, accounts for almost 40% of the total national grain and 65% of the national rice production in China.[11,12] From 1980 and 2010, the total amount of N inputs to crop production in the Yangtze basin has doubled and N use efficiencies of crop production decreased considerably from 32 to 23%.[13−15] Dissolved inorganic N (DIN) loads in the Yangtze showed a sharp increase in the past 30 years, on account of multiple anthropogenic discharges.[16] Several studies have demonstrated that intensive crop production contributed more than half of DIN loads in the Yangtze, where synthetic fertilizers were the major N source since 1990.[16−19] However, the contribution of different crops to N pollution in the Yangtze is not well studied. Unlike other rivers in the world, the Yangtze River basin is a typical basin with more than eight predominant crops and 20 rotations.[12,20] For instance, the Mississippi River basin is only cultivated with crops predominantly in a corn−soybean rotation.[21] Insights into the contribution of different crops to N pollution in rivers is essential to develop effective nutrient management options for basin with multiple crops and rotations.

Water quality models are useful tools to assess the pollution status (e.g., pollution hotspots and their sources) at different

Received: March 6, 2020
Revised: August 28, 2020
Accepted: August 28, 2020
Published: August 28, 2020

https://dx.doi.org/10.1021/acs.est.0c01333
Environ. Sci. Technol. 2020, 54, 11929−11939

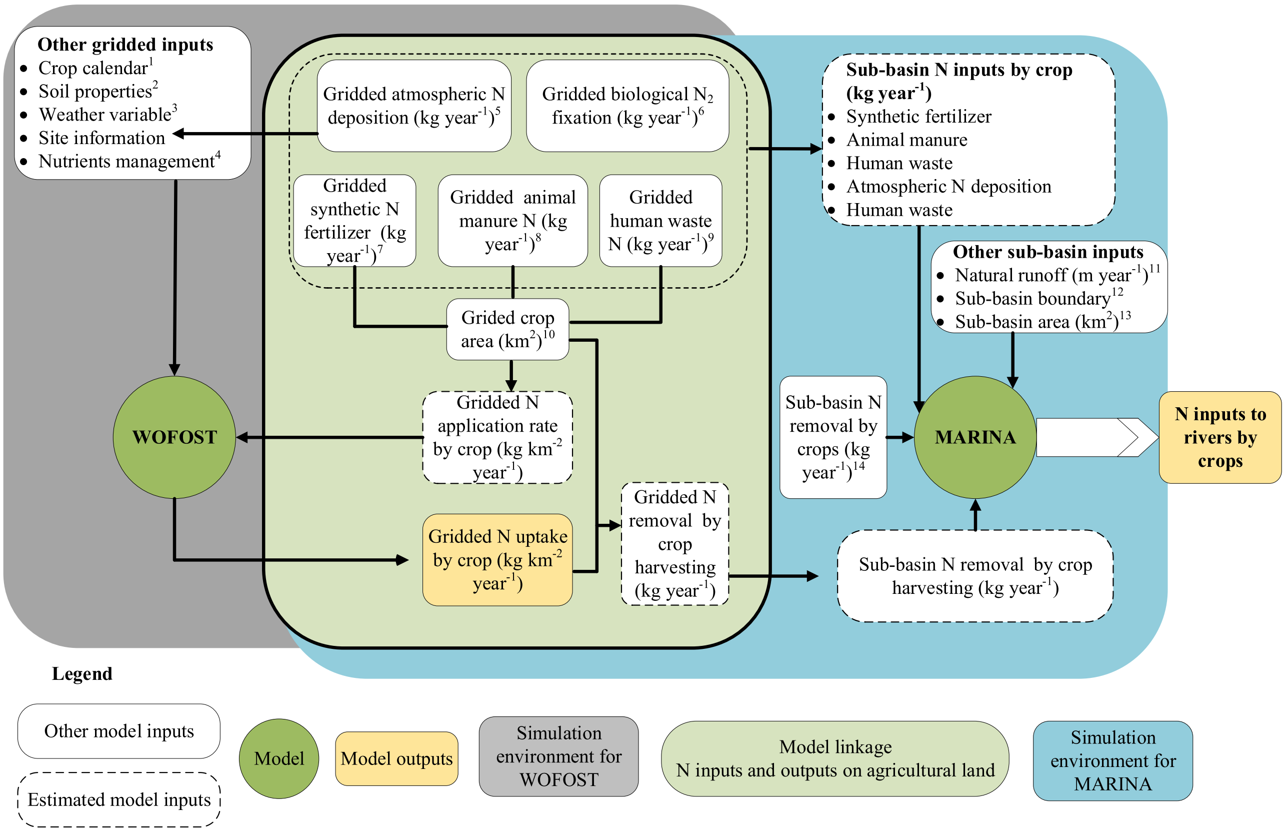


Figure 1. Framework of the new MARINA-WOFOST model system. In this framework, we consider version 2.0 of the MARINA model. MARINA is short for a Model to Assess River Input of Nutrient to seAs.[27] WOFOST is short for WOrld FOod Study.[26] The superscript numbers (1−14) in the figure refer the sources of inputs to the MARINA-WOFOST model system. More details about the sources of the model inputs are listed in Table S1.

temporal−spatial scales and explore solutions to support policymaking to improve water quality.[22] Such models include diffuse sources of N in rivers resulting from crop production. Examples of these models are the Global Nutrient Export from Watersheds 2 (Global NEWS-2) model[23] and Integrated Model to Assess the Global Environment-Global Nutrient Model (IMAGE-GNM).[24] In 2016, Strokal et al.[19] developed the first version of the Model to Assess River Input of Nutrient to seAs (MARINA 1.0) for China. It is the sub-basin version of Global NEWS-2. There are more versions of the model available for the Chinese rivers: 1.1 (Chen et al.), 2.0 (Wang et al.), and 3.0 (Chen et al.). These existing versions differ in the spatial (3.0 for multiscale and 2.0 for sub-basins) and temporal (e.g., 1.1 for seasons and 1.0 for annual) levels of detail. All versions of the MARINA model have updated information for reservoirs and include sources of N in rivers that are specific for China (e.g., direct discharges of animal manure and human excreta). However, all existing MARINA models are only capable of quantifying N inputs to rivers from aggregated sources such as the use of synthetic fertilizers, animal manure on land, direct discharges of manure to rivers, sewage systems (source attribution). These sources are not crop-specific. The existing models often do not distinguish the contribution of individual crops and their spatial variability to quantify DIN inputs to rivers. The SPAtially Referenced Regressions On Watersheds (SPARROW) model can take into account the difference in the share of crops to the total N inputs to rivers[25] but not for DIN and not for sub-basins of the Yangtze River. On the other hand, existing crop-specific models such as WOrld FOod Study (WOFOST)[26] are capable of quantifying the N cycle between crops and soil. However, they are either too detailed (e.g., in time and space) for large basins and/or hardly quantify inputs of N to rivers.

Clearly, the contribution of different crops to N pollution in rivers is not well studied, especially for large basins such as the Yangtze. A modeling approach that includes crop-specific sources (e.g., cereals, cash crops) as well as N-specific sources (e.g., fertilizers, manure) is needed, in particular, for the large basins such as the Yangtze with multiple crops and rotation systems. Thus, the main objective of this study is to improve our understanding of the contribution of different crops to N inputs to rivers. To this end, we linked the MARINA 2.0[27] model and the crop WOFOST model.[26] The resulted MARINA-WOFOST linked model system quantifies DIN inputs to rivers by crops at the sub-basin scale. On the basis of data availability in MARINA 2.0, we applied this new MARINA-WOFOST model system to the Yangtze River basin (Figure S1) for the year 2012 as an illustrative example.

2. MATERIALS AND METHODS

2.1. MARINA 2.0. The MARINA 2.0 model is a sub-basin scale model that can quantify annual dissolved inorganic and organic N from land to sea in China for 2012.[27] It is an improved version of the existing MARINA 1.0[19] model with updated information for the year 2012 and future. The MARINA 2.0 model quantifies river export of nutrients as a function of nutrient inputs to rivers from diffuse and point sources and retention of nutrients in rivers. It quantifies N

https://dx.doi.org/10.1021/acs.est.0c01333
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inputs to rivers as DIN from agricultural land by N-related agricultural sources, but without specifying the contribution of individual crops to N pollution in rivers. The N-related agricultural sources in the model are synthetic fertilizers, animal manure, human waste, atmospheric N deposition, and biological N_2 fixation.

In the MARINA model 2.0, Wang et al.[27] divided the Yangtze basin into 11 sub-basins to better reflect the spatial variation in nutrient export. These sub-basins include Jinsha, Min, Wu, Jialing, Upper stem, Dongting, Han, Poyang, Middle stem, Downstream, and Delta (Figure S1). These sub-basins are further classified as upstream, middlestream, and downstream. Jinsha, Min, Wu, and Jialing are tributaries in the upstream of the Yangtze basin. These upstream tributaries drain into the main channel, called the Upper stem. Dongting, Han, and Poyang belong to the middlestream tributaries. The Middle stem receives water from the Upper stem and middlestream tributaries. The Middle stem and Downstream sub-basins drain into Delta, a downstream sub-basin. Nutrients from the downstream sub-basin enter directly the East China Sea.

2.2. WOFOST. WOFOST is a universal and process-based model that can simulate the growth of 22 crops at a daily scale but excludes vegetables and fruit trees.[26] The simulation processes of crop growth include, for example, phenological development, CO_2 assimilation, transpiration, respiration, partitioning of assimilates to the various organs, and dry matter formation under the local conditions of soil, meteorology, water management, and agronomy management. WOFOST includes different configurations of the crop growth simulation: potential production simulation (limited by crop variety, radiation, and temperature) and water and nutrient-limited situation (nutrient and/or water shortage limits crop growth).[28] In this study, the configuration of nutrient-limited production is considered. More details of the model description can be found in earlier studies.[29,30]

In this study, we used the WOFOST model to simulate N uptake by single rice, early rice, wheat, maize, beans, cotton, rapeseed, and potato in the Yangtze River basin for the year 2012 at the 0.5° grid scale. To implement WOFOST at the grid scale of 0.5°, we followed the approach of Boogaard et al.[31] Climate, soil, and crop variables are assumed to be homogeneous within a grid (0.5 × 0.5°). We collected gridded information on weather, soil, and crop variables for the Yangtze basin. The details of inputs data for WOFOST can be found in Section S3. When all of the above data was collected, we ran WOFOST to derive the crop yield and N uptake by individual crop type per square kilometer. We converted this data to grids of 0.5°. The gridded amounts of N uptake for different crops were quantified by multiplying by N uptake per square kilometer from WOFOST with the crop area (see Figure S4 for the source). Gridded values were used as inputs to MARINA 2.0 (Figure 2; details can be found in Section 2.3).

2.3. MARINA-WOFOST Model System. In this study, we present a new model system by linking MARINA 2.0[27] and WOFOST[26] (Figure 1). This model system aims to quantify the amount of N inputs to rivers as form DIN from crop production by N-related agricultural and crop-specific sources. Rivers referred to all of the streams of water flowing in the sub-basin. MARINA 2.0 and WOFOST are soft-linked; e.g., outputs of WOFOST are used as inputs to MARINA and vice versa (see Figure 1). Below, we specify how to implement the MARINA-WOFOST model system for the Yangtze (Figure 1).

In this study, we first quantified N inputs to individual crops from various N-related sources at a 0.5° grid for the Yangtze River basin using existing data sets (more details are in Section S2). Then, we quantified the amount of DIN that is reaching rivers from different crops (e.g., wheat, maize) and different sources (e.g., fertilizers, manure). In the Yangtze, crop-related sources of N inputs to rivers include the production of single rice, early rice, late rice, wheat, maize, beans, cotton, rapeseed, potato, vegetables, fruit trees, and other crops. Other crops include managed grass, peanut, sugarcane, and other cereals. Crop-related and N-related agricultural sources are linked. For example, the production of cereals (crop-related sources) can receive N from synthetic fertilizers, animal manure, and atmospheric N deposition (N-related agricultural sources). Thus, N inputs to rivers result from synthetic fertilizers, animal manure, and atmospheric N deposition from the production of cereals.

To account for the crop attribution in DIN inputs to rivers, we improved the MARINA 2.0 model. The main equations to quantify DIN inputs to rivers by crop are as follows (modified from MARINA 2.0[27])

$$\mathrm{RSdif}_{\mathrm{DIN}.y.\mathrm{ant}.j.i} = \mathrm{WSdif}_{\mathrm{N}.y.j.i} \times \mathrm{G}_{\mathrm{N}.j.i} \times \mathrm{FE}_{\mathrm{WS.DIN}.j} \quad (1)$$

$$\mathrm{G}_{\mathrm{N}.j.i} = 1 - \frac{\mathrm{WSdif}_{\mathrm{N.ex}.j.i}}{\mathrm{WSdif}_{\mathrm{N.fe}.j.i} + \mathrm{WSdif}_{\mathrm{N.ma}.j.i} + \mathrm{WSdif}_{\mathrm{N.hum}.j.i} + \mathrm{WSdif}_{\mathrm{N.dep.ant}.j.i} + \mathrm{WSdif}_{\mathrm{N.fix.ant}.j.i}} \quad (2)$$

$$\mathrm{FE}_{\mathrm{WS.DIN}.j} = \mathrm{Rnat}_j^{\mathrm{aDIN}} \times \mathrm{eF} \quad (3)$$

where $\mathrm{RSdif}_{\mathrm{DIN}.y.\mathrm{ant}.j.i}$ is the DIN inputs to rivers in sub-basin j from N-related agricultural source y and crop-related source i (kg year^{-1}). $\mathrm{WSdif}_{\mathrm{N}.y.j.i}$ is the N inputs to crop i in sub-basin j from source y (kg year^{-1}). $G_{\mathrm{N}.j.i}$ is the fraction of N applied to crop i that is retained in soils after crop harvesting in sub-basin j (0−1). $\mathrm{FE}_{\mathrm{WS.DIN.j}}$ is the fraction of N entering rivers as DIN (0−1), quantified as a function of annual runoff from land to streams in sub-basin j (Rnat_j, m year^{-1}). Rnat_j was obtained from the Variable Infiltration Capacity (VIC) hydrological model.[32] aDIN is a constant that is used in the function of runoff, and eF is a watershed export constant (details are in Mayorga et al.[23]). $\mathrm{WSdif}_{\mathrm{N.fe}.j.i}$, $\mathrm{WSdif}_{\mathrm{N.ma}.j.i}$, $\mathrm{WSdif}_{\mathrm{N.hum}.j.i}$, $\mathrm{WSdif}_{\mathrm{N.dep.ant}.j.i}$, and $\mathrm{WSdif}_{\mathrm{N.fix.ant}.j.i}$ refer to the amount of N inputs to crop i from synthetic fertilizers, animal manure, human waste, atmospheric N deposition, and biological N_2 fixation in sub-basin j, respectively (kg year^{-1}). The sub-basin N inputs to crop i from N-related agricultural sources are aggregated from 0.5° grid data sets to 11 sub-basins of the Yangtze (the details are specified in Section S2).

The model system accounts for N removal by crop harvesting ($\mathrm{WSdif}_{\mathrm{N.ex}.j.i}$, kg year^{-1}). This N removal is generated by WOFOST in combination with existing data sets (Figure 1). The N removal from harvested single rice, early rice, wheat, maize, beans, cotton, rapeseed, and potato was taken from WOFOST (described in Section 2.2). The 0.5° gridded amount of N removal by harvesting or grazing for vegetable, fruit trees, peanut, sugarcane, and other cereals were

https://dx.doi.org/10.1021/acs.est.0c01333
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quantified using the crop yield, N content in the crops, and the sown area of the crops. The yields of vegetables, fruit trees, peanut, sugarcane, and other cereals per square kilometer were quantified using the total yield divided by the total area at the provincial scale from the National Bureau of Statistics of China.[33] We assigned the provincial values to 0.5° grids by assuming the yield of all grid cells in the province to be consistent. The yield of managed grass was a national average value without variation between grids, derived from the Nutrient flows in Food chains, Environment and Resource use (NUFER) model.[34] The N content in grains of vegetables, fruit trees, peanut, sugarcane, and other cereals was obtained from NUFER.[34] The gridded sown area of crops is specified in Section S1. Finally, we aggregated the 0.5° gridded amount of N uptake by individual crops to the sub-basins of the Yangtze as inputs for $WSdif_{N.ex.j.i}$ (see eqs 1–3).

2.4. Model Performance. In this study, we used the two models (MARINA and WOFOST) that have been evaluated for their performance in earlier studies.[19,35,36] We linked these models and added the crop attribution for DIN inputs to rivers. In this study, we further evaluated the performance of the MARINA-WOFOST model system in the simulation of crop yields and DIN inputs to rivers of the Yangtze River basin.

First, we compared modeled crop yields from WOFOST with statistical data sets at the provincial scale for the Yangtze (Figure 2). The statistical crop yield was obtained from the National Bureau of Statistics of China.[33,37] We took the available data of crop yield (kg ha^{-1}) for the provinces that covered the Yangtze River basin (Figure S1). The modeled crop yield (kg ha^{-1}) for each province was quantified by averaging values over the grids within a corresponding province (Figure S6). The performance of WOFOST was assessed using the following statistical indicators: the coefficient of determination (R^2), Nash–Sutcliffe model Efficiency (NSE) coefficient, and relative error (RE). R^2 indicates the proportion of the total variance in the statistical data that can be explained by the model.[38] The range of R^2 is from 0 to 1. NSE is used to describe how well the statistical versus modeled data fits the 1:1 line,[39] within the range from $-\infty$ to 1. R^2 and NSE indicate a good agreement between statistical and modeled values when the values are closer to 1. RE indicates how large the error of simulation is relative to the correct value. We defined RE as the ratio of the absolute error of the averaged simulated yield to the average statistical yield.

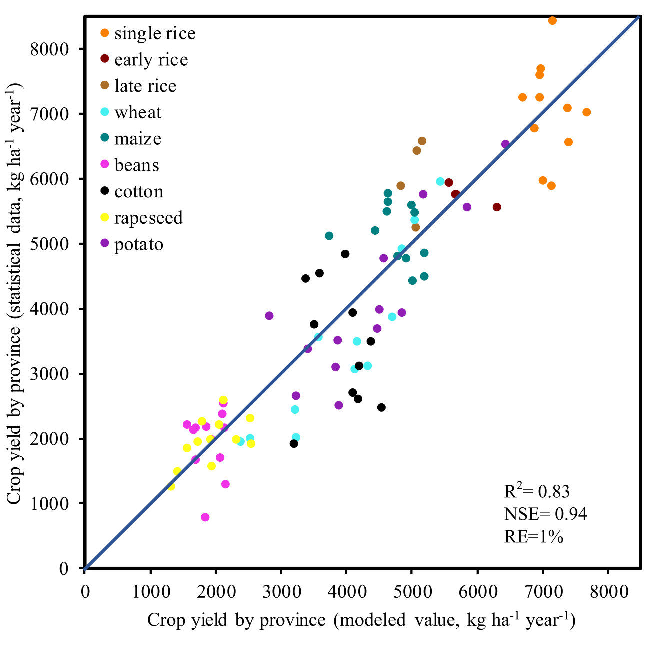

Figure 2. Comparison of the crop yield by province for the Yangtze River basin between the statistical data set for China and modeled values from WOFOST for the year 2012 (kg ha^{-1} year^{-1}). The blue solid line in the graph indicates a 1:1 line. NSE is the Nash–Sutcliffe model Efficiency coefficient. R^2 is the coefficient of determination. RE is the relative errors. WOFOST is short for WOrld FOod Study.[42] Source: The statistical data set is from the National Bureau of Statistics of China in 2012. The modeled values are from the outputs of the WOFOST model for crop yields (see Section 2.2).

The comparison of modeled and statistical crop yield has the following results: 0.83 for R^2, 0.94 for NSE, and 1% for RE (Figure 2). These results indicate that our modeled crop yield has a good agreement with the provincial statistical data from China. The deviation from the 1:1 line for some individual crops can be attributed to uncertainties in model inputs (more details see in Section 3.3).

Second, we evaluated the performance of the MARINA-WOFOST model system by comparing our results with modeled results from other studies.[23,40,41] The comparative result indicates that the MARINA-WOFOST model system has an acceptable performance in quantifying N inputs to rivers for the Yangtze. Detailed discussions on our model comparison are available in Section 3.3.

3. RESULTS AND DISCUSSION

3.1. Nitrogen Inputs to Different Crops in the Yangtze River Basin. Inputs of N to land in the Yangtze basin differ among the 12 crops (Figure 3A). Approximately 18 000 Gg of N was applied to the production of 12 crops in the Yangtze basin in 2012 (Figure 3A). This amount resulted from synthetic fertilizers, animal manure, human waste, atmospheric N deposition, and biological N_2 fixation. Two-thirds of this amount was applied to single rice (2310 Gg year^{-1}), wheat (2621 Gg year^{-1}), maize (1873 Gg year^{-1}), potato (1562 Gg year^{-1}), and vegetables (3,880 Gg year^{-1}). The remaining part was applied to early rice (672 Gg year^{-1}), late rice (748 Gg year^{-1}), beans (523 Gg year^{-1}), cotton (439 Gg year^{-1}), rapeseed (1136 Gg year^{-1}), fruit trees (1171 Gg year^{-1}), and other crops (1014 Gg year^{-1}) in the Yangtze River basin (Figure 3A). Inputs of N to most crops were mainly from the application of N synthetic fertilizers in the basin except for beans and other crops (Table S3). For beans and other crops, biological N_2 fixation was an important source of N on the land in the basin. The application of animal manure contributed only 11% to the total N inputs to the land, while half of that was applied to vegetables (Figure 3A). Animal manure was also applied to grow fruit trees and potatoes but in lower amounts than for vegetables (Table S2).

Inputs of N to different crops showed a large spatial variation (Figure 3B). N inputs to land by individual crops varied from 0 to 50 Gg grid^{-1} year^{-1} among grids (0.5 × 0.5°). Obviously, several hotspot grids of N inputs to individual crops can be observed in upstream, middlestream, and downstream (Figures 3B and S1), where N inputs to individual crops were higher than 7.3 Gg grid^{-1} year^{-1} (0.9 quantile of N inputs to crops per grid). In general, N inputs to most crops only exited only one hotspot area in the Yangtze. For instance, the hotspots of N inputs to the wheat and maize production only can be observed in the northern Downstream. Moreover, the

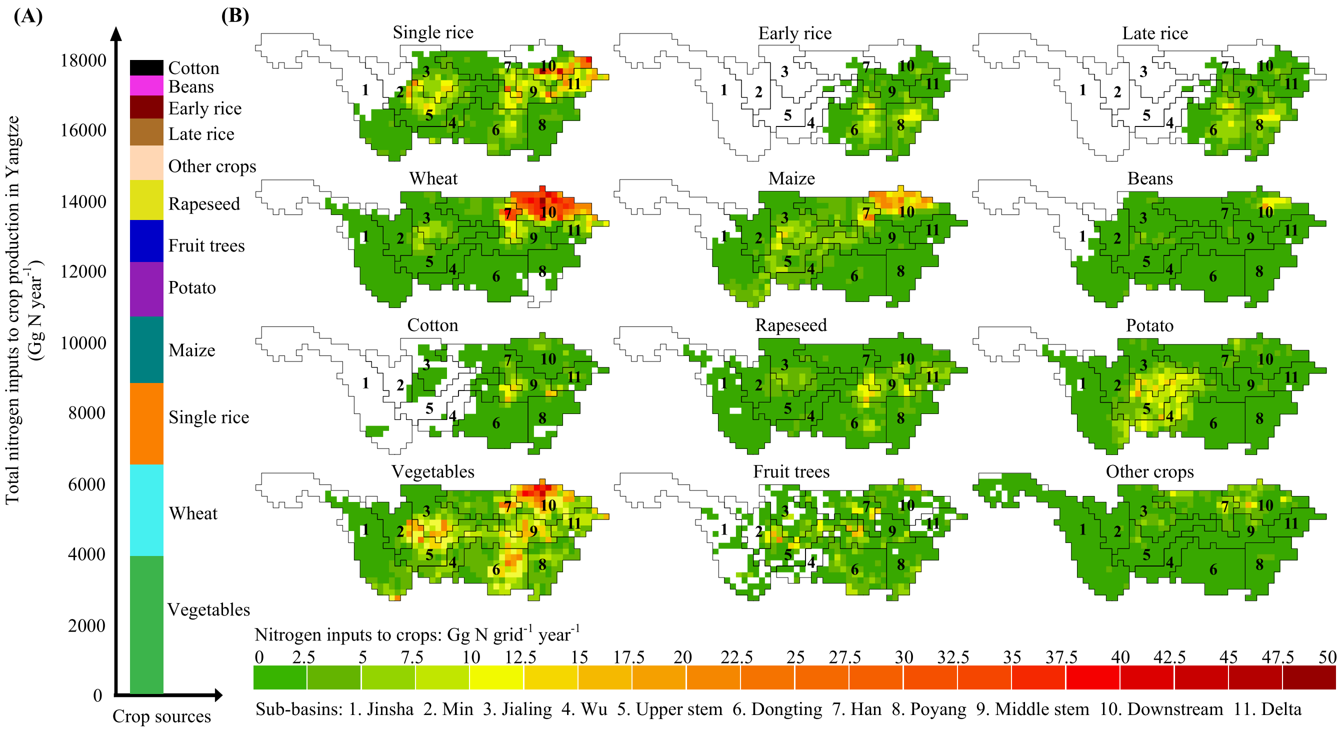

Figure 3. Nitrogen (N) inputs to crop production. (A) Total N inputs from synthetic fertilizers, animal manure, human waste, atmospheric N deposition, and biological N_2 fixation to crop production in the Yangtze River basin in 2012 (Gg N $year^{-1}$). (B) Total N inputs to different crops per 0.5° grid in the Yangtze River basin in 2012 (Gg N $grid^{-1}$ $year^{-1}$). Source: see Section S2.

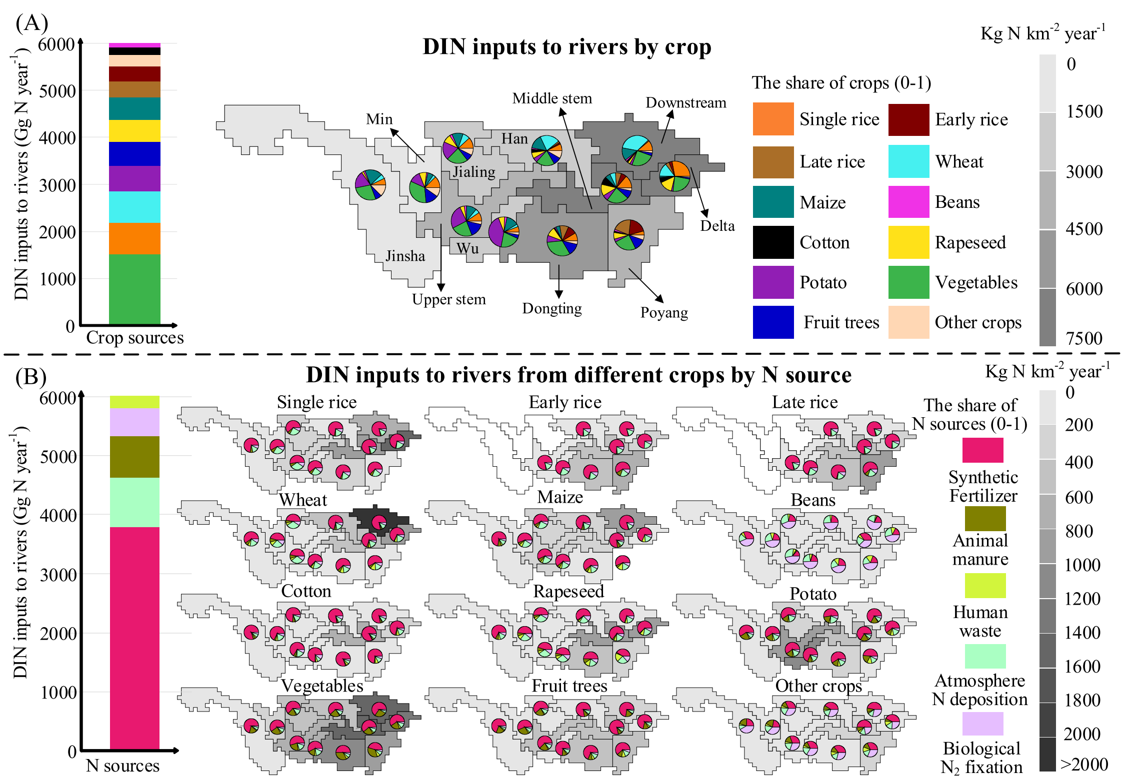

Figure 4. Dissolved inorganic nitrogen (DIN) inputs to rivers of the Yangtze basin. (A) Total amount of DIN inputs to rivers by crop-related sources (bar, Gg N $year^{-1}$) at the sub-basin scale of the Yangtze in 2012 (map, kg N km^{-2} $year^{-1}$). Pie charts show the contribution of different crop-related sources to DIN inputs to rivers (%). (B) Total DIN inputs to rivers by nitrogen (N)-related agricultural sources (bar, Gg N $year^{-1}$) and DIN inputs to rivers from individual crops at the sub-basins of the Yangtze in 2012 (maps, kg N km^{-2} $year^{-1}$). Pie charts show the contribution of N-related agricultural sources to DIN inputs to rivers from the production of individual crops (%). Source: the MARINA-WOFOST model system (see Section 2.3).

https://dx.doi.org/10.1021/acs.est.0c01333
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Downstream sub-basin contributed 62% to total N inputs to the wheat production, only covering 9% of the Yangtze River basin area. The hotspots of N inputs to the potato production were located in the upstream sub-basins (Upper stem, Wu, and southern Jialing). In comparison, N inputs to the production of single rice and vegetable existed multiple hotspot areas in the Yangtze. Except for southern Downstream and Delta sub-basins, some hotspot grids of N inputs to single rice also can be observed in the northern Upper stem and southern Jialing. This is also true for vegetable production. Besides, some hotspots of N inputs to vegetables were also found in the eastern Dongting and Middle stem. This spatiality can be explained by the spatial difference in crop sown area and N inputs rate. Generally, the sown area of crop and synthetic N fertilizer application in the hotspots was more intensive than that in nonhotspots in 2012 (Figure S4, Table S2).

3.2. Nitrogen Inputs to the Yangtze by Crops, Sources, and Sub-basins. Our results indicate that approximately 6000 Gg of DIN was exported to rivers in the Yangtze basin from crop production in 2012 (Figure 4A). Half of this amount was from the production of single rice, wheat, and vegetables (Figure 4A). These crops received N largely from synthetic fertilizers and animal manure (only for vegetables; see Section 3.1).

Three-quarters of manure-related DIN in the Yangtze were from vegetables, fruits, and potatoes in 2012. For the entire basin, animal manure only contributed by 12% to inputs of DIN to rivers from the production of all studied crops (Figure 4B). However, this is different for vegetables, fruits, and potatoes, whose production included large amounts of N manure application (see Section 3.1). As a result, the production of these crops resulted in large amounts of DIN in rivers from animal manure. However, this is different for the other crops where the use of synthetic N fertilizer was more important than the use of animal manure (Figure 4B and Table S3). We calculate that approximately two-thirds of DIN inputs to rivers from the crop production were from synthetic fertilizers (Figure 4B). Exceptions are the production of beans and other crops (Figure 4B). These crops received N largely via the biological N_2 fixation in 2012. As a result, the biological N_2 fixation was responsible for 37−57% of DIN inputs to rivers from the production of beans and for 22−42% of DIN to rivers from the production of other crops in the sub-basins of the Yangtze (Figure 4B).

The contribution of crops to DIN inputs to rivers was different among sub-basins (Figure 4A). Approximately, one-quarter to one-third of DIN in rivers from crop production were from vegetables in the sub-basins (Figure 4A). In addition to this, the production of vegetables was a dominant source of DIN inputs to their rivers, such as the Jinsha (27%), Min (33%), Jialing (23%), Dongting (32%), Poyang (24%), and Middle stem (23%) sub-basins. In these sub-basins, some other crop-related sources also contributed a prominent role in DIN inputs to rivers. For instance, double season rice (early and late rice) was a major source in Poyang, which is a typical rotation in the middlestream of the Yangtze, accounting for 40% of total DIN in rivers from crop production. For the other sub-basins (Wu, Upper stem, Han, Downstream, and Delta), the dominant crop-related sources of DIN in their rivers differed. For example, the production of potato was the dominant source of DIN in rivers of some upstream sub-basins (Wu and Upper stem in Figure 4A). The production of wheat and single rice was responsible for around half of DIN in rivers of the Downstream and Delta sub-basins. In contrast, the maize production only contributed from 12 to 20% of DIN in rivers of Jinsha, Jialing, Wu, Upper stem, Han, and Downstream sub-basins (Figure 4A). Among all sub-basins, the production of beans generated the least amount of DIN to their rivers and contributed only 1−3% of DIN inputs to the rivers in the entire basin. The spatial difference in the contribution of crops to DIN inputs to rivers can be partly explained by the spatial variability in N inputs to crops (Table S3). For instance, in the sub-basins where vegetable dominated DIN inputs to rivers from crop production, the amount of N inputs to vegetables also was the highest among all crops (Table S3).

Higher inputs of DIN to rivers per km^2 from crop production were in middle- and downstream sub-basins (2079−7029 kg km^{-2} $year^{-1}$) than in upstream sub-basins (208−3381 kg km^{-2} $year^{-1}$) in 2012 (Figure 4A). Examples of the middle- and downstream sub-basins are the Middle stem, Downstream, and Delta sub-basins. The rivers of these sub-basins received the highest amounts of DIN in 2012 (Figures 4A and S1). The rivers of Delta received the highest DIN inputs from the production of single rice (1786 kg km^{-2} $year^{-1}$) and rapeseed (917 kg km^{-2} $year^{-1}$) (Figure 4B). The rivers of the Downstream sub-basin received the highest DIN inputs from the production of wheat (2408 kg km^{-2} $year^{-1}$), maize (942 kg km^{-2} $year^{-1}$), beans (124 kg km^{-2} $year^{-1}$), and vegetables (1725 kg km^{-2} $year^{-1}$). However, there are a few exceptions. For example, the rivers of the Wu sub-basin received much higher inputs of DIN per km^2 from the potato production (1158 kg km^{-2} $year^{-1}$) than from the other crops (100−870 kg km^{-2} $year^{-1}$). This also holds for the rivers of the Upper stem sub-basin in the upstream of the Yangtze (see Figure 4B).

3.3. Model Uncertainties. To increase trust in our model results, we compared our results with other independent studies. We compared the total DIN inputs to rivers of the Yangtze (from Section 3.2 and Table 1)[23,40,41] and the total N inputs to crop production in the entire basin (Table 1).[11,12,15]

Table 1. Comparison of Nitrogen (N) Inputs to Crop Production (1000 Gg $year^{-1}$) and Dissolved Inorganic Nitrogen (DIN) to Rivers (1000 Gg $year^{-1}$) in the Yangtze River basin between This Study and Other Studies

	results	year	ref
N inputs to crop production	14.0	2010	Wang et al.[11]
	16.4	2010	Wang et al.[15]
	15.0	2012	Chen et al.[12]
	18.0	2012	this study
DIN inputs to rivers from crop production	6.4	2010	Liu et al.[41]
	3.0	2000	Mayorga et al.[23]
	6.8	2010	Liu et al.[40]
	6.0	2012	this study

Our results for N inputs to the rivers as DIN were comparable with results from other models (Table 1). In the Yangtze, Global NEWS-2,[23] IMAGE-GNM,[40] and Land Surface Model for Chinese Academy of Sciences (CAS-LSM)[23] have been implemented to quantify N inputs to rivers of the Yangtze from crop production for the years 2000, 2010, and 2010, respectively. Our estimate (6.0 Tg) was close to the estimate of CAS-LSM[41] (6.4 Tg). The minor gap can be attributed to differences in the modeling approaches. Our

https://dx.doi.org/10.1021/acs.est.0c01333
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estimate was lower than the estimate (6.8 Tg) of IMAGE-GNM. One reason is that the IMAGE-GNM simulates the N delivery to rivers from crop production as form total N. Another reason is that IMAGE-GNM assumes that all animal manure in the Yangtze River basin is recycled to cropland, reducing N inputs to rivers from manure point sources. Our results in DIN inputs to rivers for 2012 were generally higher than the results (3.0 Tg) of Global NEWS-2 for 2000.[23] This can be explained by increasing agricultural activities between 2000 and 2012.[43]

Our results for the total N inputs to crop production are also comparable with other studies (Table 1). The relatively small differences in the total N inputs to crop production between our study and existing studies can be explained by differences in basin boundaries and years. The above comparison builds trust in our approach to quantify DIN inputs to rivers from agricultural land by crop.

Although our modeled results compare well to the other studies, we still realize that our model results have uncertainties associated with the approaches, model parameters, and inputs. In our study, we used two models: MARINA and WOFOST. Both models have been widely applied and evaluated in previous studies.[18,19,27,35,36]

WOFOST has been applied to simulate the production of the main annual crops over Europe[28,44] and China.[45] It also has been evaluated against experimental information in previous studies.[31,46] However, some incomplete data sets that were used to produce model inputs may introduce uncertainties in the simulation of WOFOST for the Yangtze basin. For instance, the 0.5° gridded crop phenology was deduced with limited meteorological stations from the China Meteorological Data Service Center (Section S3).[47] We have adjusted the crop phenology in areas for which we did not have enough information. We did this by taking into account expert knowledge and temperature variation (Section S3). Soil property (e.g., soil moisture content and hydraulic conductivity of saturated soil) in the calculation of WOFOST was estimated from soil texture (Section S3).[48] We also assumed that there is only one variety for each crop type in the entire basin, which means diverse crop varieties in reality may cause uncertainties in crop yield simulation. Crop yield is essential information that is needed for the MARINA model. Although the comparison of the crop yield gives trust in using WOFOST to model crop yield for MARINA to quantify DIN inputs to rivers, the performance of the simulation for individual crops was not perfect. For instance, uncertainties remain for beans and cotton (see Figure 2, Section 2.4). Therefore, we performed a sensitivity analysis to quantify the response of total N inputs to rivers from crop production to changes in the yield of individual crops (Figure S7). We found that modeled DIN inputs to rivers were relatively insensitive to changes in the yield of individual crops. This implies that the uncertainties in the yield of individual crops do not influence the main messages of our study.

In this study, we quantified DIN inputs to rivers from different crops as a function of surface runoff and N budgets for different crops, following the approach from MARINA 2.0.[27] The existing versions of the MARINA model were validated and evaluated on national,[19,27] basin[19,27] and sub-basin scales[18] in China. MARINA 2.0 was validated at the river mouth by comparing the modeled concentrations in 2012 with observed including the Yangtze River.[27] Validation results (e.g., R^2 = 0.85) build trust in using the model for N pollution assessment.

However, model uncertainties in the MARINA-WOFOST model system are related to simplifications of N losses from soils to rivers. In our model system, we account for N losses from soils due to, for example, denitrification processes. We, however, realize that N export from land to rivers could also be influenced by several other factors, such as soil slope, soil texture, and vegetation coverage.[49−52] These factors differ among sub-basins and crops in the Yangtze River basin. These factors are lumped in the MARINA model to quantify DIN inputs to rivers from crop production. This is a simplification but does not influence our main conclusions because DIN inputs to rivers are more sensitive to variations in precipitation (natural runoff) and N inputs to land.[53] In our model, we account for these two important factors. For example, we use the widely used VIC hydrological model[32] that considers changes in precipitation when calculating runoff.

Other sources of uncertainties are model parameters and inputs in the MARINA-WOFOST model system. For example, two parameters (aDIN and eF in Section 2.3) are taken from Global NEWS-2.[23] These parameters are used to quantify N retention in soil.[23] Chen et al.[54] tested the sensitivity of DIN inputs to rivers to changes in model inputs in MARINA 2.0. DIN inputs to rivers are relatively sensitive to changes in runoff, synthetic fertilizer, and manure applied on land. Runoff is one of the essential model inputs. The VIC model provides runoff. This model has been evaluated using daily observed records of the streamflow for 1,557 stations worldwide.[55] County synthetic fertilizers and animal manure consumption are taken from the NUFER model (for more details, see Section S2). NUFER is developed for China and provides the county-scale information that is most complete for agricultural activities and required by MARINA.[43] We derived most model inputs from this model for the Yangtze River basin (for more details, see Section S2). The crop-specific application rate of synthetic fertilizer and animal manure is also derived from official statistics of China.[56] This implies that important model inputs of our MARINA-WOFOST model system reflect the Chinese situations for the Yangtze River basin. This supports the use of our model system for N pollution assessment in the Yangtze River basin.

3.4. Strengths and Limitations of Our Model Systems and Results. We consider this study to be innovative in three main aspects. First, we present a new model system: MARINA-WOFOST. This is a unique system because it integrates crop, soil, and weather characteristics with N pollution of rivers in a spatially explicit way. It combines the strengths of both models: MARINA (water quality model) and WOFOST (crop model). This combination of models makes it possible to quantify crop-specific sources of N pollution in rivers. This was not possible in earlier versions of the MARINA model. Second, our analyses of the model results for the Yangtze provide new insights into nitrogen pollution of that river. We provided quantitative estimates for the contributions of various crops to N pollution in rivers. To our knowledge, this is the first attempt to quantify the contributions of crops to N pollution in rivers of the Yangtze. Third, our study is the first to provide spatial details for crop-specific pollution in the Yangtze basin. We showed the differences in DIN inputs to rivers from crop production among sub-basins. We also analyzed the contributions of crops to nitrogen pollution at the sub-basin scale. This has not been done before for the Yangtze basin and improved our understanding of crop-specific sources. For instance, we learned that the production of double season rice (early rice and late rice) contributed 40% to DIN inputs to rivers of sub-basin Poyang, while the production of wheat and maize were the major contributors (50%) to DIN inputs to rivers of the most polluted sub-basin in the Yangtze (Downstream).

Our study also has limitations. Our model system quantifies N inputs to rivers from crops but not the resulting water quality (e.g., concentrations of N). As a result, we cannot validate our model by comparing the pollution loads to water quality parameters directly. Calculating DIN concentrations in rivers would require a quantitative assessment of all emissions (e.g., point source of manure discharge and wastewater treatment plants) and N retention in rivers and reservoirs. This is not included in the current version of the model. Nonetheless, our results can improve our understanding of the differences between crops in N pollution of water systems. We consider that these results highly relevant for setting priorities in nutrient management for crops. Another limitation is that we do not account for the possible effects of climate change. Climate change can alter the magnitude of N inputs to rivers from cropland by changing surface runoff. For instance, extreme rainfall events in the Yangtze basin in 2020 could enhance N inputs to rivers. We also need to realize that our modeled year 2012 may differ from the present situation. The sown areas and application of N-containing fertilizers among crops may have changed since 2012,[5] in response to recent policy regulations.[57,58] Therefore, the share of crops in the N inputs to rivers from cropland in 2020 is likely different than that in 2012. It would be interesting to apply this model in future studies to other years as well following our methodology.

3.5. Policy Support and Future Outlook. The Yangtze River Economic Belt in China aims toward green development: sustainable production of crops with low environmental impact.[59] In 2018, the National Development and Reform Commission and four other ministries in China jointly issued a document, entitled "Guiding Opinions on Accelerating the Promotion of Agricultural Diffuse-Source Pollution Control in the Yangtze River Economic Belt".[60] This document sets the targets to reduce synthetic fertilizer consumption by 3−5% between 2015 and 2020 while increasing yields. For the Poyang and Dongting sub-basins, this reduction is 10%. Our results provide insights into the contribution of crops to N pollution in the Yangtze. These insights can support policymakers to formulate effective, crop-specific solutions to reduce N pollution in a spatially explicit way (sub-basins). Such policies can focus on dominant crop-related sources. For instance, our results indicate that the production of wheat and maize was the major contributor to DIN inputs to rivers of the most polluted sub-basin in the Yangtze (Downstream). This was mainly due to the overuse of synthetic fertilizers to grow these crops. This implies that improved nutrient management in the wheat and maize production will likely reduce DIN pollution in rivers of that Downstream sub-basin. In this example, reducing the overuse of synthetic fertilizers to wheat and maize can be one of the policy priorities for reducing N pollution in rivers of the Downstream sub-basin.

According to the results of MARINA 2.0,[27] crop production contributed approximately 50% to DIN inputs to the Yangtze. Crop area is particularly important in the Middle stem, Delta, and Downstream sub-basins, where crops contributed by as much as 70% to DIN inputs (Table S7). Jinsha and Min are exceptions with lower contributions. Crop production will remain a key sector in mitigating DIN loads in the Yangtze and its tributaries because the discharge of point source pollution has been strictly controlled in recent years.[61] In our study, we soft-linked MARINA with the WOFOST model (Figure 1). WOFOST can further be used to explore the crop-specific management (e.g., fertilization timing and amount) to support policies that aim to mitigate DIN in rivers. For example, WOFOST can help to determine optimal N inputs for wheat and maize in the Downstream sub-basin. Analogously, WOFOST can also help to identify the recommended date of sowing and fertilization for wheat and maize to optimize growth and improve yield by accounting for local climate conditions. The Ministry of Agriculture of China (MOA) introduced technical guidance on fertilization in spring and fall from 2011 for several major grain-producing areas in China, including the Yangtze River basin.[62] The proposed measures included recommended amounts and methods of applying synthetic fertilizers and animal manure to main crops based on the target yield. All of these policy recommendations were introduced for the entire basin. Our insights can facilitate the formulation of crop-specific reduction options that consider variations among and within sub-basins (Figures 3 and 4). MARINA quantifies the DIN inputs to rivers of the Yangtze under different crop-specific nitrogen management scenarios. However, for local analysis, our model system needs to be further evaluated. Besides implications for future environmental policy formulation, our approach also provides possibilities to assess the impact of current policies in crop production on N pollution in rivers. For instance, China released the National Structure Adjustment Plan for Crop Production (2016−2020) in 2016.[58] They intend to expand the area planted to rapeseed in the middlestream and downstream of the Yangtze and to potato and other cereals in the upstream while replacing the maize production with managed grass in Jinsha. The DIN exported to rivers varied between crops (Figure 4B). These variations can also be involved in the MARINA-WOFOST model system.

To conclude, we developed a new model system to quantify DIN inputs to rivers of the Yangtze sub-basins by crop-related and N-related agricultural sources for the year 2012 (Figure 1). The novelty of our work is in the linking of the MARINA 2.0 model on river quality with the crop model WOFOST for the first time. Our results highlight the importance of considering the contribution of crops to river N pollution. Half of the DIN exported to rivers from crop production in the Yangtze in 2012 is from single rice, wheat, and vegetables. Across the entire basin, the major N-related agricultural source is synthetic fertilizers. Animal manure contributes a relatively small share of DIN inputs to rivers (12%), of which three-quarters are from vegetables, fruits, and potatoes. The contributions of crops to DIN exported to rivers differ among sub-basins. For instance, in the Wu and Upper stem sub-basins, potatoes dominate DIN inputs to rivers from crop production. Furthermore, our results provide new insights into manage river pollution from crop production by clarifying the combined information on the contribution of various crop-related sources and N-related agricultural sources. Our approach can be wider applied to other river basins where then N pollution in rivers is dominated by agricultural activities as in the Yangtze, such as Mekong River[63] and Indus.[64]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c01333.

Sown area per crop and grid of 0.5° (Section S2 S1), nitrogen inputs to land per crop and grid of 0.5° (Section S2), inputs for crop growth in WOFOST (WOrld FOod STudy) (Section S3), and sensitivity analysis (Section S4) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Key Research and Development Project of China (No. 2016YFD0200104), the National Key Technology Research and Development Program (No. 2015BAD06B04), the State Cultivation Base of Eco-agriculture for Southwest Mountainous Land, Southwest University China (No. 5330200076), and the Chongqing Scientific Innovation Project for Postgraduates, China (CYB18090). We also would like to acknowledge the contribution of Yahui Gong for the graphic abstract.

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https://dx.doi.org/10.1021/acs.est.0c01333
Environ. Sci. Technol. 2020, 54, 11929−11939