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Assessment of nitrogen budget in detailed spatial pattern using high precision modeling approach with constructed accurate agricultural behavior

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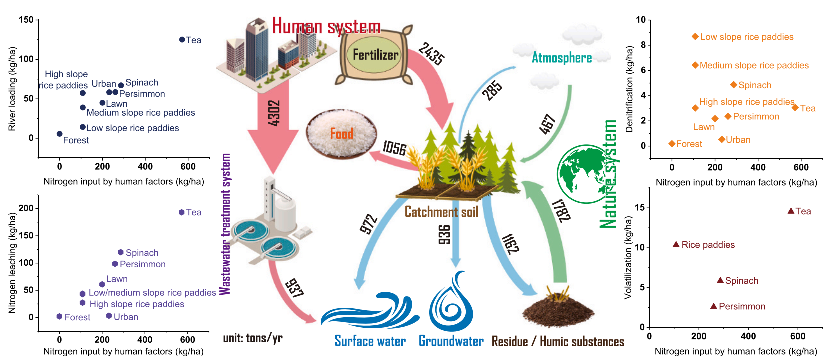
HIGHLIGHTS

- Fertilizer use correlates positively with N leaching and denitrification.
- N leaching in upland fields is higher than in rice paddies within a unit area.
- Paddies with flat terrain and ample soil water are prone to denitrification.
- Landsat-PAET is more suited to study paddy evapotranspiration than MODIS.
- Calibration of concentration obtains more accurate results than that of flux.

GRAPHICAL ABSTRACT



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ABSTRACT

Changes in the nitrogen cycle due to fertilizer use can cause severe environmental pollution, particularly groundwater pollution, and threaten biosphere integrity. There are many difficulties and limitations in assessing groundwater pollution and a detailed nitrogen budget in an agricultural catchment. Previous methodologies have failed in an accurate assessment of the nitrogen budget in detailed spatial patterns. Herein, we designed a new modeling approach to assess the nitrogen budget using detailed spatial patterns in an agricultural catchment in the Nara Basin. We revised the Soil and Water Assessment Tool file output format, added the results for river nutrient concentrations and ammonia volatilization to the original output file. In this study, we calibrated and validated crop harvests, paddy evapotranspiration, streamflow, and river water concentrations of nitrate–nitrogen and total nitrogen to improve model accuracy as much as possible. Among them, data for evapotranspiration was obtained from a newly released Landsat dataset. The results showed that the amount of nitrogen leaching in rice paddies was 42 kg/ha, accounting for 65 % of total leaching in the study catchment. Cambisols and Fluvic Gleysols were prone to denitrification, and nitrogen leaching or denitrification occurred relatively more readily in low-slope areas. Furthermore, a detailed analysis of nitrogen cycle processes with high spatial precision indicates that areas with severe surface water pollution may also exhibit significant groundwater

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pollution. Our findings provide new solutions for assessing the nitrogen budget and groundwater pollution in catchments.

1. Introduction

Anthropogenic factors dominated by fertilizer usage have perturbed the material cycle patterns represented by nitrogen (N), probably doubling the turnover rates of the terrestrial N cycle (Gruber and Galloway, 2008; Galloway et al., 2008; Aguilera et al., 2021). Changes in the N cycle patterns pollute the hydro-environment and threaten biosphere integrity (Steffen et al., 2015; Wang et al., 2021a; Tedengren, 2021). Erosion caused by soil scouring from precipitation leads to nutrient loss and is a major cause of environmental pollution (Wang et al., 2022a; Wang et al., 2021b; Malagó et al., 2017). Nitrogen that cannot be absorbed by plants leaches into aquifers and contaminates groundwater (Malagó et al., 2017; Van der Laan et al., 2014; Stuart et al., 2011), aggravating water pollution (Van Meter et al., 2017). Groundwater plays an important role in both terrestrial and marine ecosystems (Taylor et al., 2013; Luijendijk et al., 2020). Assessing the N balance, particularly groundwater contamination, is crucial for protecting terrestrial and marine environments.

Septic tanks are a major source of N contamination of groundwater and have been linked to groundwater contamination in coastal areas (Reay, 2004; Howard and Gerber, 2018; Shukla and Saxena, 2020). Owing to increased fertilizer usage, N leaching in agronomic soil results in a steady increase in groundwater N concentrations (Kumazawa, 2002; Wang et al., 2019). Assessing N leaching in spatial detail on a large scale is useful for elucidating N pollution in groundwater but methodological difficulties remain. The most used method for measuring groundwater quality is a sampling approach to quantify nutrient concentrations in samples (Constantin et al., 2011; Onishi et al., 2012), which when combined with isotopic tracers tracks N transport and transformation (Nikolenko et al., 2018). With the development of modeling techniques, crop models, e.g., cropping systems simulation models and root zone water quality models, have been used to analyze groundwater contamination from agricultural sources (Van der Laan et al., 2014; Li et al., 2020). They assess the groundwater quality of a specific area or N cycling in plants but cannot assess groundwater contamination in detailed spatial patterns on a large scale, e.g., various land-use and soil types on the catchment scale.

Non-point source (NPS) pollution models effectively estimate the process and quantity of NPS pollutants entering water bodies (Adu and Kumarasamy, 2018). The Soil and Water Assessment Tool (SWAT) is a semi-distributed NPS pollution model that considers the impact of rural and agricultural management (Adu and Kumarasamy, 2018). The N cycle module of SWAT considers each process affecting N content in agronomic soils, including fertilizer and manure application, N_2 fixation by legume plants, plant uptake, volatilization, denitrification, leaching, and erosion (Neitsch et al., 2011). A Hamadan–Bahar catchment study estimated nitrate (NO_3^-) leaching based on land uses and soil types. Nitrate estimations exhibited large uncertainties despite efficient streamflow simulations (Akhavan et al., 2010). A study on a tributary of Chesapeake Bay using SWAT to assess annual N leaching on the catchment scale demonstrated the feasibility of assessing groundwater contamination using SWAT (Hively et al., 2020). Another study on the Suwannee River catchment proved that SWAT simulates N management on a field scale (Rath et al., 2021), suggesting that improvements in the physical reality of the model, including the definition of agricultural behavior, calibration, and validation, can help simulate N pollution in groundwater.

The traditional calibration method for N flux cannot simulate the N cycle. As nutrient flux is a calibrating and validating target, its calibration results are dominated by the streamflow, and changes in nutrient concentrations may be overshadowed by satisfactory results for streamflow (Arnold et al., 2012; Moriasi et al., 2015). There are many “black-box processes” in SWAT, which involve the use of the SWAT algorithm. Users cannot check the calculation results of these steps from the output file, hindering their understanding of the overall N cycle.

Herein, we designed a systematic approach to improve the physical reality of the model (available data) and open the “black-box limitation” in SWAT to study the N budget in detailed spatial patterns on the catchment scale. The following questions were addressed: What are the main drivers of N leaching and denitrification? How does N from anthropogenic and natural systems cycle at the catchment scale? Is groundwater pollution from agricultural sources more serious than river water pollution? Our methods and findings provide new solutions for assessing the N budget and groundwater pollution in catchments.

2. Materials and methods

2.1. Study area

The study catchment in the Nara Basin covers an area of approximately 714 km^2 and represents a food-producing area in Western Japan since the 1600s (Fig. 1a), particularly famous for persimmon (Ukita, 1957; Doi, 2010). The forest area accounts for 39.2 %, with half being evergreen forests (Fig. 1b). Rice paddies account for 20.5 %, and other fertilized soils, including orchards, upland fields, tea land, and lawn land, account for 2.9 %. The annual data for the Nara Prefecture show that the main agricultural product of orchard land is persimmon, and the main farm product of dry fields is spinach (https://www.pref.nara.jp/6437.htm). Herein, we defined an agricultural behavior database for orchards and dry fields based on persimmon and spinach fields, respectively. Residential buildings represent 28.0 % of the basin. As most local houses are Japanese-style single-family buildings, their pervious surfaces account for ~50 % of the total residential area. Many families use it as a home garden (Wang et al., 2021c). The basin has four soil types, i.e., Fluvic Gleysols (45.4 %), Regosols (29.3), Cambisols (13.2), and Acrisols and Luvisols (12.1 %), with Fluvic Gleysols being the main soil in rice paddies. Annual precipitation during the study period was 1556 mm.

2.2. Weekly sampling and nutrient analysis

The study catchment harbors four water quality stations and a hydrologic station managed by the Ministry of Land, Infrastructure, Transport and Tourism (MLIT) and two wastewater treatment plants (WWTPs) managed by the Nara Prefecture (Fig. 1c). However, there is only one water quality station (at the outlet of sub-basin No. 3) located upstream of the two WWTPs, rendering it difficult to enable an accurate calibration of NPS loading of N. To increase the sample size of upstream river water samples affected by NPS pollution alone, we set up two observation points for assessing river water quality at sub-basin Nos. 6 and 7 on the upper reaches of the Saho River. The observation periods were from January to November 2021 and August 2020 to December 2021, respectively. Among the two observation points, the region upstream of sub-basin No. 6 covers tea land with the highest amount of fertilizer use per unit area within the study area, and sub-basin No. 7 is mainly residential land used to assess N losses from home gardens. Water samples were collected weekly, and their NO_3-N concentrations were determined by ion chromatography using a continuous-flow automated nutrient analyzer at Hiroshima University (Kimbi et al., 2021).

2.3. Constructing agricultural behavior database

Fertilization exerts a very important effect on the environment (Gruber and Galloway, 2008; Aguilera et al., 2021; Wang et al., 2022a). To quantify the fertilization process, three factors must be determined, i.e., fertilizer type, time of application, and amount applied.

In the Nara Basin, rice paddies in plains and mountainous regions exhibit different schedules due to different varieties of rice grown. Rice planted in mountains is transplanted to harvest, including fertilization, one month earlier than the rice planted in plains. In the study catchment, it was necessary to construct agricultural behavior databases for plain rice paddies, mountain rice paddies, persimmons, spinach, tea, lawns, and home gardens.

According to the reports of the Nara Prefecture Government (https://www.pref.nara.jp/8652.htm) and the local fertilizer company (https://www.i-nouryoku.com/QandA/hiryou), N fertilizers used in the study area are of three types, i.e., NO_3^-, ammonia (NH_3), and mixed fertilizers ($NO_3{-}N{:}NH_4{-}N = 1{:}1$). Ammonia fertilizer is applied to rice paddies, mixed to tea lands, and NO_3^- to all other types. Following local customs, organic fertilizers, e.g., manure, are applied to rice paddies, persimmon land, and spinach land. Nitrogen content in manure was calculated based on the N content in the wastes of different animals as assessed from livestock information (https://www.pref.nara.jp/6437.htm) (Mishima et al., 2015). The amount of fertilization and other agricultural behavior information for each land use type is shown in Table 1. Fertilizer amounts used in spinach and persimmon fields are set following the minimum amount recommended by the government. In actual agricultural activities, persimmon fields require excessive fertilization. The amount of fertilizer used needs to be calibrated. Spinach fields face excessive fertilization, as farmers top-dress based on spinach growth. We used the auto-fertilization operation of SWAT to simulate topdressing. We also used the auto-fertilization operation for residential areas regarding unquantifiable information, e.g., the fertilizer amount applied to home gardens. The maximum usage for auto-fertilization requires calibration.

2.4. Optimize SWAT to improve usability

As we know, the method utilized for nutrient calibration in the SWAT-Calibration and Uncertainty Program is predicated on flux (Neitsch et al., 2011), that is, streamflow × nutrient concentration × time step. In SWAT, as the calculation process of streamflow is simpler than that of nutrients, it is relatively more straightforward to achieve better calibration results, implying higher evaluate indicator values than those obtained for nutrients. When we multiply a high value (such as a streamflow result) and a low value (such as a nutrient concentration result), we get a value in the middle (such as a nutrient flux result), implying that nutrient calibration will be affected by the high-value results of streamflow and cannot be accurately judged. Therefore, the calibration of nutrient concentrations can yield relatively more reliable results than those obtained with the calibration of nutrient fluxes.

Based on the above reasoning, we modified the SWAT output file to calibrate the nutrient concentration in the channel. The revised work was based on SWAT 2012 rev. 681 and coded in Microsoft Visual Studio 2019 with Intel oneAPI 2021.

As N calibration is a target for river water quality, new print data must be added to the river channel (RCH) output files of the SWAT. Four files needed to be modified, i.e., rchday.f, rchmon.f, rchyr.f, and rchaa.f,

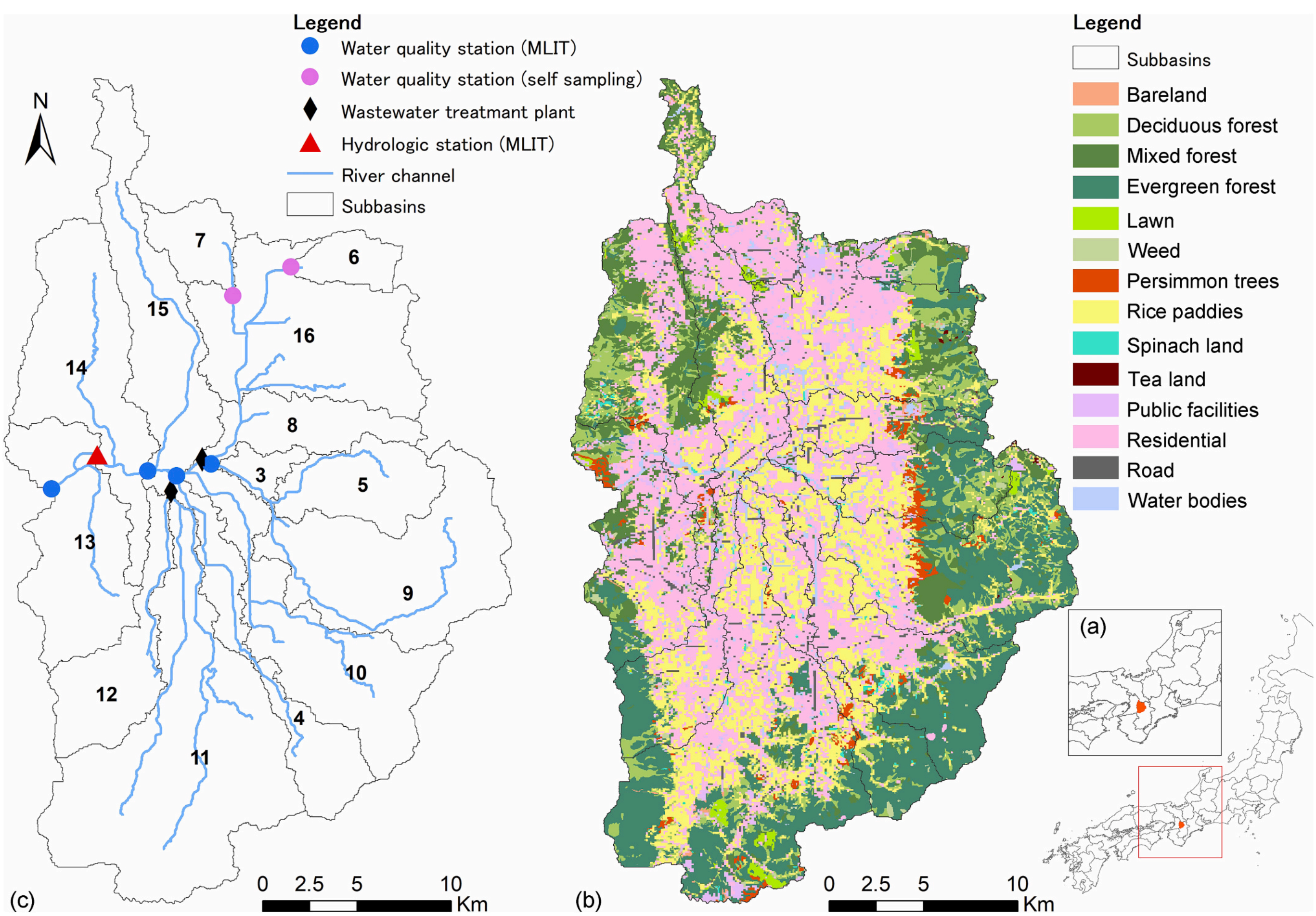

Fig. 1. Catchment location (a), land use (b) and Gauging station distribution (c) of Nara Basin.

Table 1
Preset catchment agricultural behavior database.

	Rice (plain)	Rice (mountain)	Persimmon	Spinach (rotation 1)	Spinach (rotation 2)	Tea	Residential (home garden)	Lawn
Plant/begin growing season	May	Apr	Mar	Mar	Sep	Mar	Apr	Mar
Fertilizer type	$NH_4{-}N$	$NH_4{-}N$	$NO_3{-}N$	$NO_3{-}N$	$NO_3{-}N$	$NO_3{-}N$ $NH_4{-}N$	$NO_3{-}N$	$NO_3{-}N$
Fertilization frequency and period	Jun, Aug	May, Jul	Dec, Jul, Oct	Mar	Sep	Feb, Apr, Jul, Aug	April	Mar, May, Jul, Aug
Total N applied (before calibration) (kg N/ha)	108	108	180	115	115	572	30	200
Total N applied (calibrated value) (kg N/ha)	/	/	260	143.5	143.5	/	16.5	/
Harvest/wither season	Oct	Sep	Nov	May	Dec	May, Jun, Jul	Sept	Oct

which correspond to the data output of daily, monthly, yearly, and period averages, respectively. Because the original SWAT file has already output the streamflow and nutrient flux results under the corresponding time scale, we only need to add the following equation to the file to output the river water nutrient concentration:

$$N_{conc} = N_{fo} / F_{out} / T / 1000, \tag{1}$$

where N_{conc} is the average nutrient concentration during the time step (mg N/l), N_{fo} is the nutrient quantity transported with water and out of reach during the time step (kg N), F_{out} is the average streamflow out of reach during the time step (m^3/s), and T is the time step factor. As N_{fo} is the accumulated nutrient flux within a certain time and F_{out} is the average flow during that period, it must be divided by T to obtain the average nutrient concentration.

Another part that needs to be modified is the NH_3 volatilization calculation module of the SWAT. The default SWAT output file covers most aspects of the N cycle, including plant uptake, denitrification, erosion loss, and leaching. However, NH_3 volatilization is not included in the output file. This is because the variable *rvol* for NH_3 volatilization is a local variable in this module that is reset after each execution of the module code, rendering the results of NH_3 volatilization unviewable to the user. In this study, we summarized the results of NH_3 volatilization according to different land-use types in the SWAT using the following equations:

$$voln_{LU} = voln_{LU_0} + rvol \times \left(a^j_{hru} / a_{LU}\right), \tag{2}$$

$$voln_{LU_{out}} = voln_{LU} / yrs, \tag{3}$$

where $voln_{LU}$ is the average amount of N lost through NH_3 volatilization in target land use types (cumulative amount during the simulate period) (kg N/ha); $voln_{LU_0}$ is the $voln_{LU}$ value result in the last run, and its initial value should be set as 0; *rvol* is the amount of N lost from the NH_3 pool due to volatilization (kg N/ha); a^j_{hru} is the area of the current hydrologic response unit (HRU; ha); a_{LU} is the total area of the land use type to which the current HRU belongs (ha); $voln_{LU_{out}}$ is the annual average amount of N lost through NH_3 volatilization in target land use types (kg N/ha); and *yrs* is the length of simulation (years). It should be noted that the variable $voln_{LU}$ needs to be defined in modparm.f, rewind_init.f, and zeroini.f and must be assigned an initial value of 0. Eqs. (2) and (3) should be written in the nitvol.f and writeaa.f files, respectively, and the relevant result output format requirements are defined in the stdaa.f file.

Based on these modifications, we can obtain the average concentrations of $NO_3{-}N$ and total N (TN) during unit timestep in the RCH output file (.rch), which can be used for model calibration and severity. Simultaneously, NH_3 volatilization values for different land use types can be obtained in the summary output file (.std).

2.5. Execution model, calibration, and validation

SWAT requires terrain data (https://earthexplorer.usgs.gov/) to delineate watersheds, using land use distribution (https://nlftp.mlit.go.jp/), soil distribution and attribution (https://nlftp.mlit.go.jp/), and slope (calculated based on terrain data) to delineate HRUs. The study area was divided into 16 sub-basins with 1242 HRUs. The land use, soil, and slope filters were set to 0/0/0 to maintain the complete division of HRUs. Different agricultural schedules were defined for agricultural land HRUs in the catchment based on different land use types and slope bands (Table 1). We collected meteorological data (https://www.jma.go.jp/) for 6 years from 2016 to 2021, of which the first 3 years were used as warm-up years. The point-source loading was calculated from the respective water quality records of the two WWTPs, and the average daily loads were input into the model. In this study, calibration and validation were all run on a daily scale because daily calibration and validation exhibit a better performance for the precipitation response than when run monthly (Wang et al., 2021b).

We designed the model calibration based on the material flow method (Wang et al., 2022a), represented using the following equation: N input − plant N uptake − surface N loss = N entering the atmosphere + N leaching into aquifers. The calculation of N input required detailed agricultural information, whereas the calculation of plant N uptake and surface N loss required the calibration of crop yield and river water N transport, respectively. Nitrogen entering the atmosphere and N leaching into aquifers cannot be calibrated directly, but the reliability of the value can be improved by calibrating evapotranspiration based on streamflow calibration.

First, we manually calibrated the crop yields of rice, persimmon, spinach, and tea and compared them to the actual crop yield data from the Nara Prefecture Statistical Yearbook by adjusting the plant growth parameters in the vegetation database (https://www.pref.nara.jp/6437.htm). Notably, the output mentioned in the Statistical Yearbook refers to the "commercialized yield." For rice and tea, the "commercialized yield" can be considered "dry weight." For spinach and persimmon, the "commercialized yield" must be considered "fresh weight." As the crop growth reported in SWAT is presented in dry weight, the spinach and persimmon yields reported in the Yearbook need to be converted to "dry weight" and then compared with the SWAT output. Based on crop moisture content, the fresh weight of spinach is nearly 10 times its dry weight (Kawazu et al., 2003), and the fresh weight of persimmon is roughly 5 times its dry weight (NII, N., 1980). Crop calibration was performed on averages, i.e., comparing the 3-year average of all HRUs for the same crop type with the 3-year average recorded in the Yearbook. The parameters calibrated in this step reflected the energy response and nutrient uptake during growth. The purpose of this step was to bring the plant phenology closer to the real situation in the study area.

Second, we calibrated and validated streamflow and paddy evapotranspiration (ET). We used daily streamflow data from the streamflow gauging station at the outlet of the 14th sub-basin in 2019 for calibration and in 2020 for validation. We chose Landsat Collection 2 Provisional Actual Evapotranspiration Science Product (Landsat-PAET) as the calibration data of paddies ET, which has a spatial resolution of 30 m. We used Landsat PAET data from 2019 for calibration and 2020–2021 data for validation. The parameters calibrated in this step reflect the response of the catchment hydrological processes to precipitation. The purpose of this step was to make the catchment water budget closer to the real situation because the soil water conditions are highly related to the paddy N budget.

Third, we calibrated the NO_3-N concentration of river water at three upstream observation points (Nos. 3, 6, and 7) and validated at three downstream observation points (Nos. 10, 13, and 15). The 6th and 7th sub-basins are located in residential areas and are very helpful for quantifying fertilizer application and N loss in home gardens, the biggest uncertainties in this study. The observation points of the third, sixth, and seventh sub-basins were located upstream of the two WWTPs. The 10th sub-basin observation point was located downstream of one of the WWTPs. The 15th sub-basin observation point was located downstream of both WWTPs. The 13th sub-basin observation point was the watershed outlet of the study catchment. Such a spatial distribution is helpful for detailed quantification of the spatial pattern of the N budget in a catchment. To ensure the accuracy of the model, we validated the TN concentration for river water at the watershed outlet. The performance of the model was evaluated by determining its coefficient of determination (R^2), Nash–Sutcliffe efficiency (*NSE*), and the percentage of bias (*PBIAS*) (Moriasi et al., 2015). With R^2 ranges between 0 and 1, the larger the value of R^2, the better the simulation performance of the model. Notably, *NSE* is the most popular hydrological model efficiency indicator, with ranges between $-\infty$ and 1. The value of $NSE > 0$ suggests a model with improved predictive skills (Nash and Sutcliffe, 1970). The *PBIAS* is used to measure the difference between the simulated and measured values and has an optimal value of zero (Gupta et al., 1998). After calibration and validation, the details of N flows within each process in the N cycle can be obtained from HRU output files.

3. Results and discussion

3.1. Model performance evaluation and uncertainty analysis

3.1.1. Simulation results of streamflow and N concentration

As shown in Fig. 2a, the simulated crop yield was close to the actual yield, and the rice yield was consistent with the actual constant. Fig. 2b and c show the simulation results for rice paddy ET and streamflow, respectively. According to the performance evaluation criteria summarized by Moriasi et al. (2015), the performance indicators of R^2 and *NSE* of the streamflow in the calibration and validation period reached the standard of “good” or “very good,” and the *PBIAS* of all periods reached “very good” (Table 2). The average groundwater recharge can be obtained from SWAT output files after calibration and validation. We compared groundwater recharge in the Nara Basin. The groundwater recharge obtained using this model was slightly lower than that observed in the early 1990s (Taniguchi, 1994). Considering the impact of land use changes over the past 30 years, the water balance results of the model are credible (Doi, 2010). Although there is no specific performance standard for ET, because the streamflow reached a high-performance standard and the three indicators of ET exhibit considerable values, the results of rice field ET are reliable. Herein, we found that Landsat PAET was generally higher than the SWAT-simulated value in the rainy season and slightly lower than the SWAT-simulated value in the dry season, the main manifestation of the inadequacy of the current Landsat PAET product, also mentioned in another study (Senay et al., 2023). We found that the Landsat PAET and MODIS ET data show an opposite trend of divergence. MODIS generally underestimates and overestimates ET during the wet and dry seasons, respectively (Wang et al., 2022b). Although Landsat-PAET and MODIS ET have different data performances, the 30-meter spatial resolution of Landsat-PAET is relatively more usable than the 500-meter MODIS ET. A spatial resolution of 500 m is difficult to use for dynamic monitoring under the requirement of high spatial resolution, and a spatial resolution of 30 m enables dynamic analysis at high spatial resolution. It is expected that Landsat-PAET will play a role in precision agriculture and related hydrological research.

The final performance evaluation criteria recommended by Moriasi et al. to evaluate the modeling performance of N simulations are only for evaluating monthly simulations (Moriasi et al., 2015). In addition, Moriasi et al. developed separate interim performance evaluation criteria based on different time steps, including daily simulations. The *NSE* in interim daily performance evaluation criteria was defined as “satisfactory” when >0.25, “good” when >0.4 and “very good” when >0.55 (Moriasi et al., 2015), whereas the criteria for R^2 and *PBIAS* could not be separated into different time steps owing to the lack of samples. Based on their performance indicators for NO_3-N concentrations in the calibration and validation period, R^2 and *NSE* mostly reached the standard of “satisfactory” or “good,” the *PBIAS* of all periods mostly reached “very good,” and all indicators of TN concentrations in the validation period reached the standard of “very good.” Our simulation results for N transport in the river channel are reliable and demonstrate the feasibility of using the SWAT model to assess N budgets at the catchment scale.

3.1.2. Home garden usage rate and over-fertilization in upland field

The biggest uncertainty in this study, the actual fertilizer usage in home gardens and upland fields, was also determined during the simulation process. The calibrated amount of fertilizer used in the home garden was 45 % lower than the pre-set value (Table 1). This does not imply that the amount of fertilizer used in residential areas within the catchment is 16.5 kg/ha and instead implies that, in residential areas, excluding the natural N cycle, the extra N added to the soil by humans was equivalent to 16.5 kg/ha in this model. For persimmon and spinach, the amount of fertilization in the dry fields was higher than the initial value we set. Many studies have pointed out that overfertilization commonly occurs in upland fields in Japan (Komamura, 1990; Ishihara, 1990; Fujitomi et al., 2004; Wada and Tanahashi, 2017), and the results of this study confirmed this point. It is worth noting that the auto-fertilization function will be applied to crops in perfect timing with the necessary amount when the crop experiences the stress of nutrient deficiency (Neitsch et al., 2011). This is too optimized compared to a real situation. Farmers do not apply it many times as accurately as the model calculations and maybe only once or twice. This implies that the actual amount of fertilizer could be greater than the amount applied by the function.

3.2. Nitrogen budget at detailed spatial patterns

3.2.1. Nitrogen leaching

We analyzed N leaching in the study catchment at the HRU scale (Fig. 3a). The large yellow area in Fig. 3a corresponds almost exactly to the rice fields in the catchment. The amount of TN leached into the aquifer was 936 tons/year. Nitrogen leaching from the rice paddies accounted for 65 % of TN leached into the entire catchment, 41.8 kg/ha on average, basically at the same level as the results obtained in two field studies conducted in Akita and Kanagawa prefectures of Japan (Takakai et al., 2017; Kihou and Yuita, 1992). Cases exist where despite the same soil type, N leaching is different owing to small differences in soil composition details (Kihou and Yuita, 1992). Owing to data limitations, we could not reconstruct 100 % of the soil data in SWAT. Nitrogen leaching in the study catchment was twice the level of N leaching in the rice-producing areas of the Jianghan Plain and three times the level of N leaching in the rice-producing areas of the Taihu Lake region of China (Qi et al., 2020; Peng et al., 2011). The type and amount of fertilizer are usually one of the reasons, but the relatively more significant factor that causes large differences between China and Japan is water condition. The average annual precipitation in the three regions of Japan is above 1500 mm (Takakai et al., 2017; Kihou and Yuita, 1992), whereas the average annual precipitation in the two regions of China is approximately 1100 mm (Qi et al., 2020; Peng et al., 2011). Japan has a relatively more abundant groundwater source than most regions of China

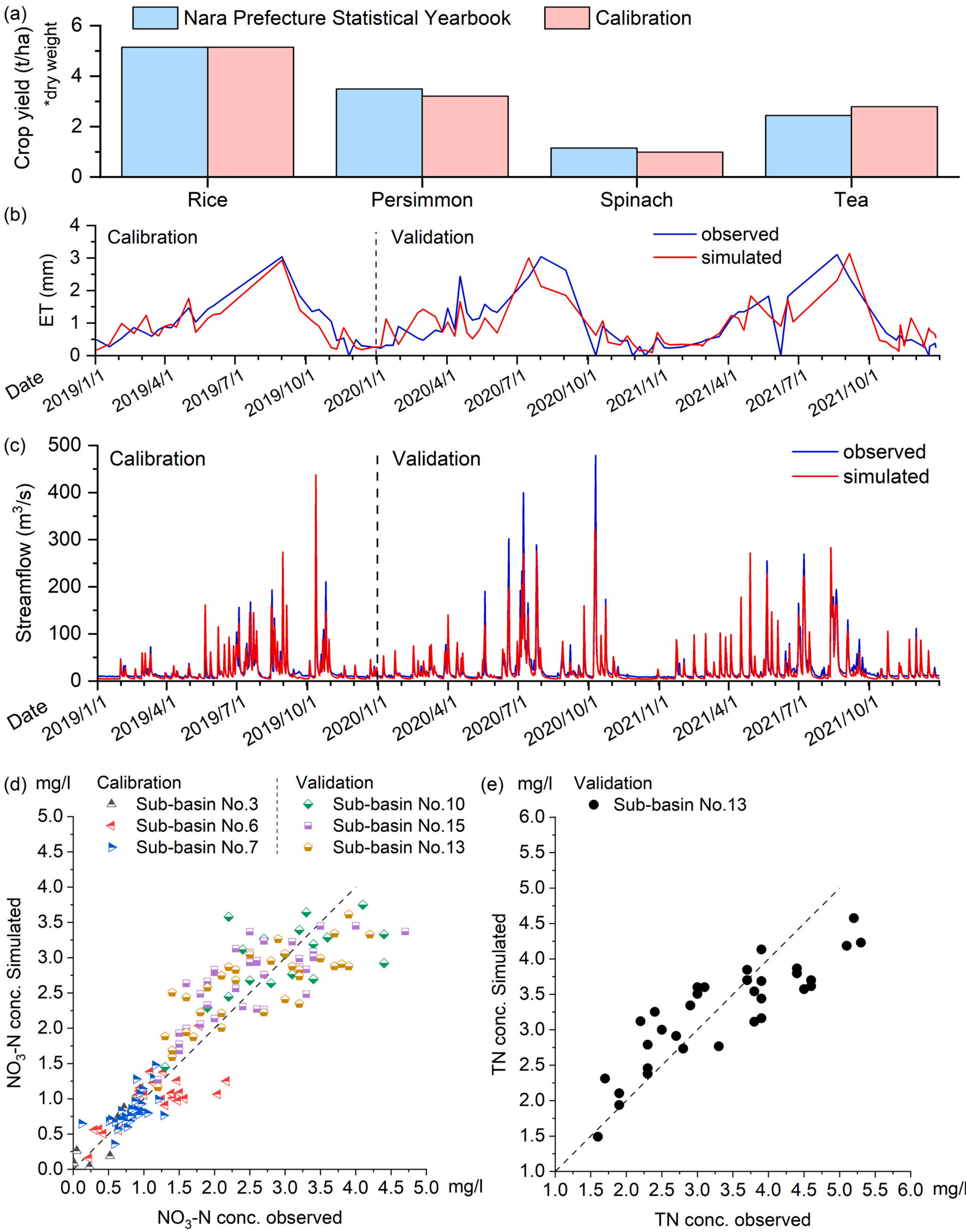

Fig. 2. Calibrated (a) crop yields, (b) paddy ET, (c) streamflow, (d) NO_3-N concentrations, and (e) TN concentrations in the revised SWAT program.

Table 2
Performance of the calibrated streamflow and nitrogen concentration in the Soil and Water Assessment Tool model (model run daily).

	R^2	NSE	PBIAS	Observed time scale
ET in plant rice paddies (Calibration/2019)	0.78	0.71	9.6	Each 16-days
ET in plant rice paddies (Validation/2020–2021)	0.64	0.61	3.5	Each 16-days
Streamflow at sub-basin #14 (Calibration/2019)	0.83 (g)	0.79 (g)	−0.4 (vg)	Daily
Streamflow at sub-basin #14 (Validation/2020–2021)	0.86 (vg)	0.86 (vg)	8.2 (vg)	Daily
NO_3−N conc. at sub-basin #3 (Calibration)	0.69 (g)	0.62 (vg)	−0.2 (vg)	Monthly
NO_3−N conc. at sub-basin #6 (Calibration)	0.51 (s)	0.44 (g)	12.1 (g)	Weekly
NO_3−N conc. at sub-basin #7 (Calibration)	0.37 (s)	0.23 (ns)	0.1 (vg)	Weekly
NO_3−N conc. at sub-basin #10 (Validation)	0.39 (s)	0.39 (s)	0.8 (vg)	Monthly
NO_3−N conc. at sub-basin #13 (Validation)	0.60 (vg)	0.55 (g)	2.1 (vg)	Monthly
NO_3−N conc. at sub-basin #15 (Validation)	0.56 (s)	0.52 (g)	−5.4 (vg)	Monthly
TN conc. at sub-basin #13 (Validation)	0.72 (vg)	0.64 (vg)	4.7 (vg)	Monthly

(vg): very good; (g): good; (s): satisfactory; and (ns): not satisfactory based on Moriasi et al. (2015).

(Gleeson et al., 2016), with a strong positive relationship between soil moisture content and N leaching (Van der Laan et al., 2014; Qi et al., 2020). Lawn land exhibited a high N leaching level at 60.9 kg/ha, contributing 4 % of TN leached into the aquifer of the entire catchment. Liquid fertilizers can sometimes cause more leaching than granular fertilizers (Tripolskaja and Verbylienė, 2014), which may be one of the reasons for the higher fertilizer usage in lawn lands than in rice paddies (Tripolskaja and Verbylienė, 2014).

Nitrogen leaching in persimmon and spinach were 98.7 and 119.9 kg/ha, respectively. Persimmon cultivation contributed 12 % of TN leached into the aquifer of the entire catchment, whereas spinach cultivation accounted for 4 %. Excessive fertilizer application is inevitable, but the type of fertilizer used may also play a role. One study pointed out that compost could lead to more serious leaching than chemical fertilizer (Choi et al., 2007), and both persimmon and spinach lands had mixed applications of compost and chemical fertilizer in the study catchment.

The highest N leaching occurred in tea land (193.0 kg/ha). Although tea land accounted for only 0.06 % of the catchment area in land use, deficiency contributed to 1 % of TN leached into the aquifer of the entire catchment, and the biggest reason was the highest fertilizer usage among all land use types. Nitrogen leaching in residential areas and forests contributed 7 %, contributed by home gardens in residential areas and forest biomass and atmospheric N deposition in forests (Fukuzawa et al., 2006; Chiwa, 2021).

3.2.2. Nitrate denitrification and ammonia volatilization

The estimated average annual NO_3^- denitrification of rice paddies

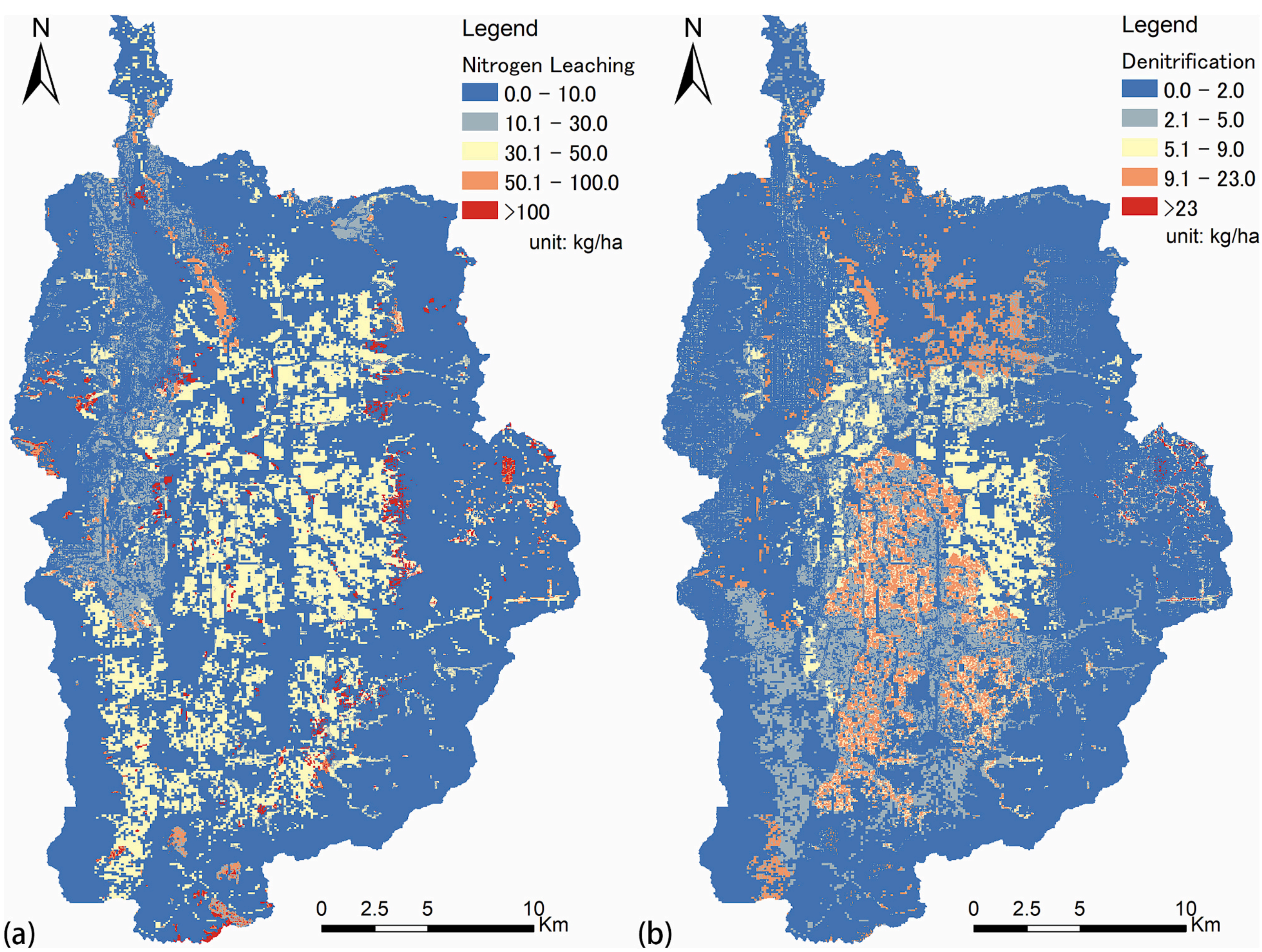

Fig. 3. Distribution map of (a) nitrogen leaching and (b) denitrification within each hydrologic response unit (kg/ha).

and spinach, persimmon, lawn, and tea lands were 7.3, 4.9, 2.4, 2.2, and 3.1 kg/ha, respectively (Fig. 3b). As the denitrification in rice paddies was higher than that in other land-use types, we analyzed the impact of different slope conditions on the denitrification of rice paddies on the HRU scale. The results showed that denitrification in plain areas reached 8.7 kg/ha but was only 3.0 kg/ha in steep mountain areas. The average value of rice paddy denitrification in the study catchment was slightly higher than the results obtained by two field studies conducted in the Kyoto and Akita prefectures (Onishi et al., 2012; Takakai et al., 2017). There are two reasons for this difference, the first is soil temperature. The activity of denitrifying bacteria decreases under low soil temperatures (Stanford et al., 1975), and the average soil temperatures in Nara Prefecture are higher than that in Kyoto and Akita Prefecture, and this difference reaches 3–4 °C in some areas (Saito et al., 2013; Owada, 1969). Groundwater is also an influential factor. According to data from the MLIT, the groundwater level is 45 m in the Nara Plain but 63 m in the Kyoto area. Abundant groundwater maintains the soil water content at a high level, and the soil water content acts as an indirect factor expressing oxic/anoxic conditions in soil layers, resulting in high denitrification levels.

In the Kyoto study, the denitrification of rice fields in the highlands was higher than that in the lowland rice fields, contrary to the results obtained in this study (Onishi et al., 2012) because the experimental fields in Kyoto are artificial terraces, and the unique hydrological characteristics of terraces lead to a higher permeability of rice paddies located in a larger area (Onishi et al., 2012). In the study catchment, the rice paddies located in steep mountains are not continuous terraces, and owing to the altitude, groundwater levels and soil temperatures are lower than those in the plains, explaining these results. The amount of denitrification in the farming season was 85 % of the total annual amount, and 15 % of the denitrification occurred in the non-cultivating season. All areas where denitrification exceeded 9 kg/ha belonged to agricultural land, exposed to anthropogenic activities, e.g., long-term fertilizer application. All areas with denitrification exceeding 23 kg/ha belonged to Cambisols, the soil type with the highest organic matter level among all soils in the study catchment. Fluvic Gleysols exhibited significantly higher denitrification than the other two soil types because they exhibited anoxic conditions due to excess soil moisture in most cases. Denitrification is a complex process; in addition to temperature, moisture conditions, and soil type, it is also related to pH, fertilizer type and usage, and snowmelt impacts (Wang et al., 2020; Gao et al., 2020). These factors determine the extent of NO_3^- denitrification and NH_3 volatilization (Fenn and Hossner, 1985).

Ammonia volatilization is a relatively more important route of N loss in rice paddies than denitrification (Xu et al., 2012). In the study area, the annual average NH_3 volatilization in rice paddies, spinach lands, persimmon lands, and tea lands were 10.3, 5.8, 2.6, and 14.5 kg/ha, respectively. This value is higher than that reported in a field study conducted in Ibaraki Prefecture, Japan, and remains at a similar level to those reported in other field studies in Tokyo, Japan, and Vietnam (Hayashi et al., 2006; Kyaw et al., 2005; Watanabe et al., 2009), but much lower than the NH_3 volatilization levels in rice paddies in China and the Philippines (Wang et al., 2021d; Fillery et al., 1984). Fertilizer type, fertilization method, and irrigation method are the main factors determining NH_3 volatilization (Hayashi et al., 2006; Kyaw et al., 2005; Watanabe et al., 2009).

Irrigation water also carries a certain amount of N, but most of it enters the atmosphere because of denitrification, and the actual amount involved in the crop N budget is small (Kyaw et al., 2005). Therefore, N from irrigation water was not considered in this study, nor included in the denitrification results. In addition, SWAT is not capable of simulating soil N_2O emissions due to algorithm limitations (Gao et al., 2019).

3.3. *Catchment scale N flow and global perspective*

In the study catchment, the wastewater from the human system was 4302 tons/year; however, 78 % of it was filtered out through the wastewater treatment system, and only 937 tons of N was discharged into the river channel (Fig. 4). Approximately 2435 tons of N is added to agronomic soil as fertilizer every year, and approximately 65 % of it is used in rice paddies. Due to the large area of arable land in the catchment, the arable land area in the study catchment accounts for 23.4 % of the total land area, higher than the world average of 10.7 % (World Bank database, 2020), leading to fertilizers having a greater proportion of the N cycle in the study catchment than in the world average (Gruber and Galloway, 2008). Nitrogen deposition was 467 tons/year. Owing to the limitation of the SWAT algorithm, SWAT only considered wet deposition, i.e., N deposition accompanied by precipitation, and could not consider the impact of dry deposition (Neitsch et al., 2011). Nitrogen fixation is an important part of the N cycle and occurs mainly in legumes (Phillips, 1980). In Nara Prefecture, the planting area for legumes is small. The effect of N fixation was ignored in this study. The TN discharge with streamflow in the study catchment was 1909 tons/year, wherein 49 % came from point-source wastewater discharge and 40 % from arable land.

In the study catchment, N lost from rice paddies accounted for ~56 % of the total available N in the paddy soil, and that in the harvest (excluding residue) accounted for 41 % of the fertilizer input, which was slightly higher than the global average (Gu and Yang, 2022; Alam et al., 2023). Appropriate fertilizer usage in paddy fields is important for the study catchment, as excessive fertilizer input will not only reduce fertilizer use efficiency but also increase pollution (Wang et al., 2022a; Liu et al., 2016). The ratio of the nonpoint source N transported into the river channel to the total amount of N leached into the aquifer in the study catchment was 1:1. Leaching is relatively more severe in rice paddies than in nonpoint source loading, implying that catchments surface water polluted by NPS loads may also face groundwater pollution of the same or worse levels. Such catchments may include the Missouri and Mississippi River catchments in the United States; Danube, Rhine, and Seine River catchments in Europe; Yangtze River and Yellow River catchments in China; Ganges River catchment in India; Yenisei and Ob River catchments in Russia; Nile and Niger River catchments in Africa; Parana River catchment in South America; Murray River catchment in Australia; and other catchments where rice is the main crop (Reid et al., 2005; Sutton et al., 2013; Mekonnen and Hoekstra, 2015; Laborte et al., 2017). Nitrogen leaching into the aquifer is transported to the seabed via submarine groundwater discharge, severely affecting the ocean ecosystem (Santos et al., 2021). For Osaka Bay, the reason for the worst water quality during the 1970s and 1980s, in addition to N loading in rivers, may likely be groundwater pollution from agricultural sources (Wang et al., 2021a). Further studies on groundwater contamination in these catchments may help elucidate the process of offshore eutrophication influenced by terrestrial fertilizer usage and the impact of anthropogenic factors on the N cycle on the catchment and global scales.

4. Conclusions

Herein, we assessed the N budget under the significant impact of anthropogenic factors. Fertilization is the primary cause of surface water pollution, denitrification, and leaching, leading to groundwater contamination. In addition, soil characteristics, notably soil water content and topography, particularly slope, substantially affect the N budget. In the study area of Nara Plain, rice paddies represent the primary source of N leaching, averaging 41.8 kg/ha. Nevertheless, leaching in other agricultural lands remains noteworthy, mainly in tea lands. Additionally, rice paddies demonstrate denitrification and NH_3 volatilization rates as high as 7.3 and 10.3 kg/ha, respectively.

Ours is the first study to report the use of SWAT to perform a detailed evaluation of the N cycle process at the catchment scale. Herein, we adopted the new Landsat-PAET evapotranspiration dataset, modified the output results of SWAT, and used weekly river water sampling and detailed agricultural data input to maximize the reliability and accuracy

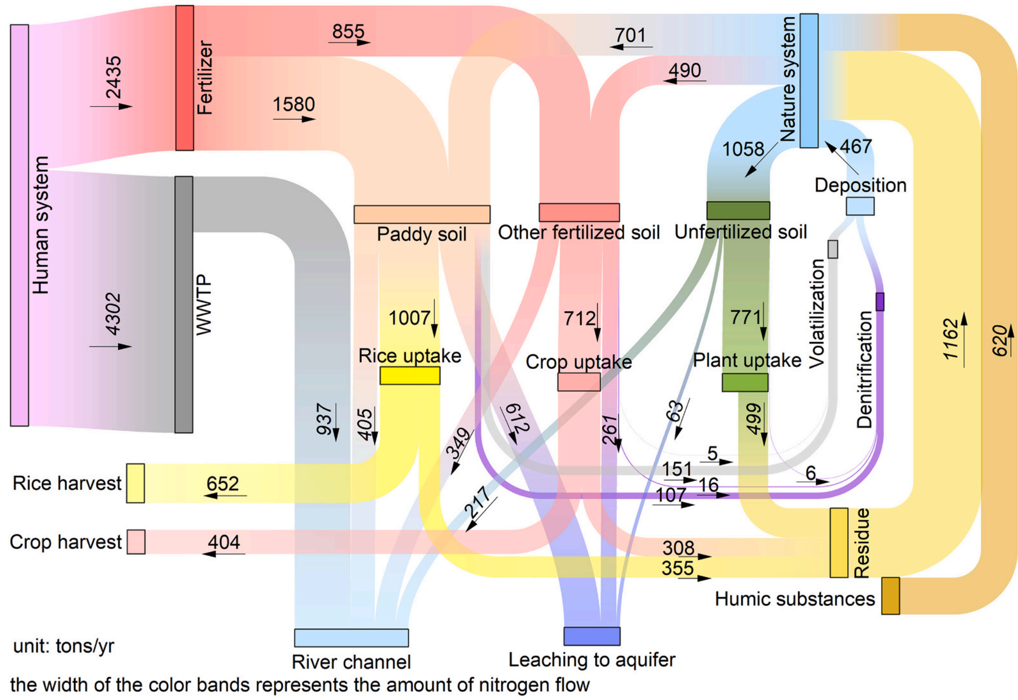

Fig. 4. Schematic diagram of the nitrogen cycle in the Nara Basin.

of the model. Using this model, we determined the values of total N input, plant N uptake, surface N losses, and NH_3 volatilization values were determined. Therefore, the results for the sum of denitrification and N infiltration are reliable; however, there is uncertainty in the respective values, mainly attributed to the quality of the soil input data, thereby affecting the precision and accuracy of the SWAT model. Nonetheless, this study presents a detailed analysis of the N cycle process at the watershed scale, particularly regarding the impact of different surface conditions (land use, soil, and topography) on the N cycle process. Herein, we also propose a highly portable catchment scale N cycle assessment method, capable of assessing in daily, monthly, and yearly time steps. In the future, we will continue to focus on the N cycle at the catchment scale, incorporating additional parameters such as changes in groundwater N concentrations and leaching lags based on recorded measurements or environmental tracer methodology to improve the model accuracy. We recommend that agricultural practitioners, particularly those engaged in upland field work, reduce the amount of chemical fertilizer usage. Excessive usage of chemical fertilizers increases expenses while also being the main cause of water pollution. In addition, the policymakers need to work with local farmers to establish a unified agricultural plan supporting local condition, ensuring economic benefits while minimizing excessive use of fertilizers and, thereby, environmental pollution.

CRediT authorship contribution statement

K. Wang, S. Onodera and M. Saito conceived of the initial idea. K. Wang improved the idea and designed the methodology and discussed with Y. Shimizu. M. Saito and S. Onodera provided the funding. K. Wang performed the modeling, validation, visualization and assessment and writes the original draft, and all authors discussed and editing, and contributed to the final manuscript.

Declaration of competing interest

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

Data availability

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

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