nature portfolio

Peer Review File

Chronic nitrogen legacy in the aquifers of China

Corresponding Author: Professor Si-Liang Li

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

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Dear Professor Li,

Your manuscript titled "Chronic nitrogen legacy in the aquifers of China" has now been seen by 2 reviewers, whose comments are appended below. You will see that they find your work of some potential interest. However, they have raised quite substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that fully addresses these serious concerns.

We hope you will find the reviewers' comments useful as you decide how to proceed. In addition, for publication in Communications Earth & Environment to be appropriate, we would need you to:
* present compelling new insights on the legacy of nitrogen pollution in aquifers and groundwater across China
* provide an extended spatial analysis of the impacts of changes in agricultural (and other) practices in China
* describe your methodology at a level of detail that an independent researcher can understand and replicate your results

Should additional work allow you to address these editorial thresholds and all the reviewers' criticisms, we would be happy to look at a substantially revised manuscript. If you choose to take up this option, please either highlight all changes in the manuscript text file, or provide a list of the changes to the manuscript with your responses to the reviewers.

When resubmitting, please provide a point-by-point response to the reviewers' comments. Please submit your responses as a separate file, distinct from your cover letter where you can add responses to the Editors' comments that you do not want to be made available to the reviewers. Word files are preferred. We recommend that any figures, tables or graphs that are included in the response to reviewers are also included in the main article or Supplementary Information.

Please bear in mind that we will be reluctant to approach the reviewers again in the absence of substantial revisions.

If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Earth & Environment or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please do not hesitate to contact us if you wish to discuss the revision in more detail.

Please use the following link to submit your revised manuscript, point-by-point response to the reviewers' comments with a list of your changes to the manuscript text (which should be in a separate document to any cover letter), a tracked-changes version of the manuscript (as a PDF file) and any completed checklist:

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Please do not hesitate to contact us if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

Somaparna Ghosh, PhD
Associate Editor,
Communications Earth & Environment

EDITORIAL POLICIES AND FORMAT

If you decide to resubmit your paper, please ensure that your manuscript complies with our editorial policies and complete and upload the checklist below as a Related Manuscript file type with the revised article:

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For your information, you can find some guidance regarding format requirements summarized on the following checklist: (https://www.nature.com/documents/commsj-phys-style-formatting-checklist-article.pdf) and formatting guide (https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf).

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

Liu et al. Groundwater legacies
Although the paper presents important data and analysis of nitrate in Chinese groundwater, I feel that there are some problems regarding the data and the analysis, a better description of the data is needed, and the analysis needs to be extended in some parts.
First the data. The observations cover the period since 2000. In that period China has gone through some dramatic changes, including population growth and agricultural intensification and also some rapid reductions of fertilizers use and wastewater discharge in the last 8-10 years as shown in Figure 5 and S5. It is not clear how the data presented reflect these changes, and how can data representing such a long period be used in combination with the spatial datasets that probably represent only one single year. For example, in the section groundwater sources: the role of soil nitrogen is important in many regions in China, and the authors present this as a form of legacy and cite the work of Van Meter et al. This implies that the accumulated soil nitrogen from centuries of application of animal manure, human excreta, other organic materials, and fertilizers in more recent times, is released by soil organic matter decomposition. This would be possible when farmers reduce the inputs of all these forms of nitrogen, and soil nitrogen is being depleted. The nitrogen released can be transported to aquifers and thus contribute to the legacy. If this is actually the case, this should be discussed as it appears to be an important consequence of the recent policy to halt the increase in fertilizer use in China shown in Figure 5 and Figure S5. The drastic change in wastewater TN and ammonia between 2015 and 2016 is also an important consequence of apparently improving wastewater treatment, although it is hard to believe such a reduction can be achieved in one year, and it is not clear how wastewater can reach the groundwater.
There is a lack of discussion of the pathways of nitrate transport in relation to the sources and also a lack of discussion of nitrate removal processes. Regarding groundwater nitrate source “manure & sewage”. It is not clear why manure and sewage are one class. Are these sources similar in terms of isotopic composition? However, the pathways for their transport are totally different. Sewage when spread on the land can move to groundwater by leaching, while sewage can move to aquifers when sewage pipes are leaking, or when human excreta are used to fertilize the land. However, the latter practice was very important in the 1970’s but is not common any longer in China at present. Also, there is a clear influence of manure and sewage on deep groundwater layers. How is this possible? This needs some more thinking and clarification.
Line 387 and onwards: this is an important observation and also needs more discussion. When denitrification is an important process, there needs to be nitrate (or other forms) and carbon forms or inorganic electron donors including reduced manganese (Mn^{2+}), ferrous iron (Fe^{2+}) and sulfides. Pyrite is the most common iron disulfide mineral in rock. It is found most often in metamorphic and sedimentary rocks where it occurs as either a primary mineral or a fine, widespread impregnation of subsequent origin. Pyrite is frequently found in association with coal and shale deposits. It is therefore interesting to analyze this further. In the data for the random forest model, one of the factors is the lithology. I was wondering if there is a relationship between nitrate concentrations and the lithology. It may not appear as a significant factor due to the method used, but if analyzed differently, it may come out as an important factor explaining nitrate removal.
Line 318-319: “abundant rainfall throughout the year facilitates the leaching of legacy nitrogen and the utilization of nitrogen fertilizer”. How can abundant rainfall facilitate fertilizer use? Many regions with a (seasonal) rainfall deficit have irrigation, so

I do not understand why only rainfall is important and irrigation has been ignored. For example, irrigation is important in the North China Plain.
The paper needs thorough editing, for example “Although there has been an overall improvement in groundwater nitrogen pollution in China since 2016” suggests that the pollution has been improved, but I guess the authors mean that pollution has been reduced or the groundwater quality has been improved. Other examples: What is the difference between aquifer depth and groundwater table. Line 134-135: higher than what? Line 203: sentence not correct? Line 187: drivers? Line 253: “drinking standard” should be “excellent water quality”. The WHO standard for drinking water is 50 mg nitrate per liter. Line 264: this further confirmed ….; why is that a confirmation?

Minor comments

Just before Line 78: how can the thickness (depth) of aquifers be inferred from wells or hand-dug holes?
Line 78-80: I think data from wells have been used elsewhere.
Line 125: what is the first number between brackets, is it the average?
Line 142: do you mean groundwater aquifers under croplands?
Table S1, for the soils data it is not clear what exactly has been used, what is the resolution, what soil depth or layer, etc etc; for the climate data: spatial resolution used?
Line 478: “To minimize the direct influence of external inputs and focus on the groundwater biogeochemical processes of nitrogen, this study excluded individual significant outliers (i.e., nitrate concentration ≥1000 mg L-1).” Totally unclear why the high values are excluded.

Reviewer #2 (Remarks to the Author):

Liu 2024 Nature - Chronic nitrogen legacy in the aquifers of China
This manuscript is generally well-written. However, I had concerns with sample collection methods, quality assurance, and consistency and integrity of the data as detailed below.
6: How were the gw sites identified and chosen and how did authors ensure that they covered the “gradients of geographical, climate, and human factors”?
14: were gw wells measured in 2016 and more recently? Were they measured once and how was variability in N quantified?
47: maybe change “is essential” to “facilitates”
58: suggest period after China
59: readers may not understand “hand-dug aquifer depth”
62: water may be pumped from the top or the bottom of an aquifer, so hand dug depth may not reveal gw table. Also, gw table can fluctuate especially in regions where gw is pumped for ag at rates higher than recharge.
65: suggest deleting “to the best of our knowledge”. We assume this is the case. Capitalize We
78: is this the proper order? Why are methods last?
Figure 1: I’m confused by the legends of the figures. Where do the legends end and the main text begin? It seems that the authors have a very long legend for the figures in which they are discussing site selection, characterization, and sampling approach. I suggest that these descriptions be placed with the methods section. For example, the study site description is embedded in the figures. I find this approach of organization confusing and does not seem standard. Suggest that the tables and figures with their respective legends be placed at the end of manuscript.
How were gw wells sampled? In what way were the data checked for consistency? In what way were the data checked for accuracy?
79: change to “at” to “in”
106: delete “it”
110: wow, that’s high! Is there NH4 data from any of these samples?
127: this description of machine learning and random forest models should be discussed in the methods section and not in the legend to fig 2.
161: I wouldn’t call aquifer depth a driver because that term implies a mechanism of action. Rather, nitrate concentration correlates with depth due to infiltration and/or or mechanisms of nitrate uptake, e.g. denitrification.
166: explain what the isotope values indicate. That is, what does a low or high value of O or N mean in this context? Do you really have isotope value for all 4000 wells? That would be difficult to accomplish. Please indicate the sample sizes associated with the isotope data across ecoregions.
170 fig 3. Why make a bar graph here instead of a continuous biplot of depth vs nitrate concentration? The categories are not indicative of anything and are contrived.
169: change drives to drivers
215: did the authors try to age date the gw for example, with CFCs, radioisotopes or other methods (e.g. Scott Phillips at USGS has done so with gw in the Chesapeake Bay region of the US).
232: poor gw at 0-18m suggests more recent inputs of N
233: still very confused about the differences among low, middle, highlands. What is important about these regions and why should the drivers be different among these 3 regions? Can the authors show land use characteristics (percentages) among these regions? Fig 4a is interesting but doesn’t give me a sense of what are the actual land use factors associated with nitrate. This representation is colorful but difficult to interpret and visualize and we don’t have the corresponding data to fully understand relationships among these factors.
254: geographic and climate factors have effects on aquifer depth? How so? What does this mean? I can understand how geography and climate affect nitrate but not the depth of the aquifer.
288: how did redox affect gw in this study? Did the authors collect data on redox?

333: how was this time comparison made? No methods are described here. Were the same wells sampled during these time periods. How were they sampled? It is speculation to say that they were significant effects due to treatment measures in 2015. What were these treatment measures? How could they have made such a large effect so quickly when previous data shown here demonstrates the chronic effects of legacy nitrogen? What mechanisms could account for such a rapid effect of management actions? No such rapid effect has been demonstrated in other regions/countries with high gw N. On line 429, the authors emphasize the fact that “nitrogen pollution control is a long-term process that does not yield immediate results due to the presence of legacy nitrogen”. How then, did the rapid change occur that is depicted in fig 5?
Fig 5: this is a very confusing figure. Why are the symbols connected by lines? This is not a time series progression but rather, these are economic regions that may or may not be connected. The important differences are the two time periods. We don’t know if the variability among time periods is small enough to indicate actual statistical differences from one time period to the next because there are no error bars and no associated statistical tests especially for 5a.
360: change intake to uptake
370: in addition to low DO, there appears to more DOC at deeper depths which could better fuel denitrification
443: when referencing the nitrogen cascade, please cite Galloway 2003. Would be useful for the reader to know what the N cascade is so that this statement has context.
456: what are the published papers? Would like to see the references and know how these wells were sampled, frequency of sampling, variability, etc.
Lit cited
Noticing inconsistent lit cited formats, e.g. 8: Nature Communications; 12 Communications Earth and Environment

Version 1:

Decision Letter:

<*** REMEMBER TO ATTACH REVISIONS CHECKLIST (WORD)***>

** Please ensure you delete the link to your author home page in this e-mail if you wish to forward it to your coauthors **

Dear Professor Li,

Your manuscript titled "Chronic nitrogen legacy in the aquifers of China" has now been seen by our reviewers, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment, provided you can show that other factors such as changes in climate, soil N, soil pH, and other dynamic soil properties do not affect the outcome of your analysis.

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. In particular, please go through the manuscript carefully to remove any inconsistent use of terms and other inconsistencies in the manuscript. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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Please review our specific editorial comments and requests regarding your manuscript in the attached "Editorial Requests Table".

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Somaparna Ghosh, PhD
Associate Editor,
Communications Earth & Environment

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

After going through the response letter, article and SI, I still have doubts about how data representing the time period 2000-2020 are used in combination with the spatial datasets that probably represent one single year. For example, population has grown by about 16% between 2000 and 2020. Probably there have been also changes in climate, soil N, soil pH, and other dynamic soil properties. I suggest that the authors show that the impact of such changes is small and can be neglected in the analysis presented, supported by literature, for all those factors that are variable.

I had a question about the lithology (which in the SI is listed under topography), and the authors responded as follows: “In this study, the random forest model data did not include lithology as a factor”. Does that mean that lithology was not considered (so why is it in the list), or did it not come out as a significant or important factor? In that case, it may be good to state that only significant/important factors are considered and to include the list of significant and non-significant factors.

A third issue which confuses me is “In addition, the RF model based on Gini index was employed to calculate the importance score of 11 variables (including GW depth, TDS, EC, MAT, longitude, ecoregion, MAP, T-water, latitude, and pH) on nitrate dynamics.” First of all, I count 10 variables in this sentence. In the methods I read the following: Here we used decision-tree heatmaps to predict the threshold values of different nitrate concentrations using the "treeheatr" package based on the interactions among aquifer depth, population density, land use, and ecoregion characteristics. In addition, the structural equation model was used to explore the occurrence regularity of nitrate dynamics under different geographical and climate factors. Geographical (including ecoregion, latitude, and longitude) and climate factors (including MAP and MAT), groundwater aquifer depth, TDS, pH, EC, and T-water were set as the variables." I see that the second list is from observations at the monitoring sites (e.g. observations), while the first list is data from the spatially explicit maps (e.g. auxilliary data, instead of "external factors" in line 272). I suggest that the authors re-organize the text and methods to make this distinction clear and to argue the purpose of each analysis.

I do not quite understand what "structural equation mode" is, and occurrence regularity". Is the structural equation model different from the RF model?

So please check this and make consistent.
Finally, the text needs serious editing by a native English speaker, also to remove inconsistent use of terms and other inconsistencies. My advice is often: try to explain this to a layman (e.g. a family member).

Reviewer Comments:

Thank you for your professional review of the manuscript. However, several problems need to be addressed. According to your nice suggestions, we have made extensive corrections to our previous draft in blue color. Please see our point-by-point responses below.

<u>Reply to Reviewer #1's major comments:</u>

Reviewer #1 (Remarks to the Author):

Liu et al. Groundwater legacies.

Although the paper presents important data and analysis of nitrate in Chinese groundwater, I feel that there are some problems regarding the data and the analysis, a better description of the data is needed, and the analysis needs to be extended in some parts.

Thank you for your constructive comments and suggestions, which have helped us to significantly improve the manuscript. Please see our response to your comments.

(1). First the data. The observations cover the period since 2000. In that period China has gone through some dramatic changes, including population growth and agricultural intensification and also some rapid reductions of fertilizers use and wastewater discharge in the last 8-10 years as shown in Figure 5 and S5. It is not clear how the data presented reflect these changes, and how can data representing such a long period be used in combination with the spatial datasets that probably represent only one single year.

Re: Thank you for your detailed feedback and for highlighting the concerns regarding the data. In this study, we compiled groundwater nitrate concentration data for different economic regions across various years, as shown in Table S5. To better capture the temporal variations, this study calculated the overall means and standard deviations (SD) for two periods: 2000–2015 and 2016–2020. This highlights the temporal variation in groundwater quality across regions. (See Lines 360-367, ***Supplementary***

***information* (SI)** Lines 207-208)

Lines 360-367:

Although the data used in this study are based on single sampling events, the data points across different economic zones are widely distributed between 2000 and 2015 and 2016–2020 (see the numbers of samples in different economic zones from 2000 to 2020 in Fig. 1a and Table S5). To better capture temporal variations, we also calculated the overall means and standard deviations (SD) for the two periods: 2000–2015 and 2016–2020 (Fig. 5). Notably, overall groundwater nitrogen pollution significantly declined during 2016–2020 compared with the data from 2000 to 2015, except in the NC and MYR (Fig. 5a).

SI Lines 207-208:

Table S5. Number of samples in different economic zones from 2000 to 2020 (N = 3163). Note: Some groundwater sampling sites do not directly provide the sampling time.

Year	NC	MYR	NE	SW	EC	NW	MCY	SC
	Number							
2000	24	37						
2001	28	18				28		
2002				52	18			
2003		16	10			10		32
2004	13	1	43					15
2005	12							
2006				25		40		23
2007				25		40		
2008	32	37		20		4		
2009	23	49		37		59		
2010	22		43		21	82	5	120
2011	54		137			135		
2012	29			41				

2013			4	26	28	13		31
2014	58	22				203		39
2015	179					17		64
2016	3			29		184		24
2017	58	23		1			13	
2018		24	9	23		38	29	
2019	42	254		22	41	44	7	
2020		50		11			90	

(2). For example, in the section groundwater sources: the role of soil nitrogen is important in many regions in China, and the authors present this as a form of legacy and cite the work of Van Meter et al. This implies that the accumulated soil nitrogen from centuries of application of animal manure, human excreta, other organic materials, and fertilizers in more recent times, is released by soil organic matter decomposition. This would be possible when farmers reduce the inputs of all these forms of nitrogen, and soil nitrogen is being depleted. The nitrogen released can be transported to aquifers and thus contribute to the legacy. If this is actually the case, this should be discussed as it appears to be an important consequence of the recent policy to halt the increase in fertilizer use in China shown in Figure 5 and Figure S5.

Re: Thank you for your valuable feedback. Based on your comments, we have revised the relevant sections to incorporate the discussion on soil nitrogen as a legacy issue, as cited in the work of Van Meter et al.'s research. This adjustment helps provide a more comprehensive explanation of the implications of accumulated soil nitrogen being released and transported to aquifers, especially within the context of recent policies aimed at reducing fertilizer use in China (See Lines 228-237).

Lines 228-237:

The high soil nitrogen contribution may reflect more samples from croplands than from other land use types (Table S4). As has been discussed extensively in literature (e.g., Van Meter, et al. [18]), agricultural lands have accumulated nitrogen originating from nitrogen fertilizers, manure, and other organic materials for decades to centuries[46]. The data here potentially indicate that these accumulations of legacy soil nitrogen contribute more to observed nitrate than the more recent addition of fertilizer and atmospheric addition. Thus, when nitrogen inputs are reduced, the nitrogen accumulated in soil organic matter may still be released and transported to aquifers, contributing to the nitrogen legacy in groundwater[18,47]. This also indicates that neglecting groundwater nitrogen isotope fractionation may lead to sources blurring and inaccurate results.

(3). The drastic change in wastewater TN and ammonia between 2015 and 2016 is also an important consequence of apparently improving wastewater treatment, although it is hard to believe such a reduction can be achieved in one year, and it is not clear how wastewater can reach the groundwater.

Re: Thank you for your insightful feedback. We revised the manuscript to address the significant changes in wastewater total nitrogen (TN) and ammonia between 2015 and 2016, emphasizing the likely improvements in wastewater treatment practices. Additionally, we have added a discussion on the challenges of achieving such rapid reductions within a single year and the uncertainties surrounding the mechanisms through which wastewater nitrogen might be transferred to groundwater (See Lines 357-369).

Lines 357-369:

Statistics indicated a consistent increase in the discharge of TN and ammonia wastewater prior to 2015 (Fig. S6). In response, the Chinese government implemented a series of comprehensive treatment measures in 2015 that effectively mitigated this trend[66], such as improving wastewater treatment. Although the data used in this study are based on single sampling events, the data points across different economic zones are widely distributed between 2000 and 2015 and 2016–2020 (see the numbers of samples in different economic zones from 2000 to 2020 in Fig. 1a and Table S5). To better capture temporal variations, we also calculated the overall means and standard deviations (SD) for the two periods: 2000–2015 and 2016–2020 (Fig. 5). Notably, overall groundwater nitrogen pollution significantly declined during 2016–2020 compared with the data from 2000 to 2015, except in the NC and MYR (Fig. 5a). This is due to the significantly deeper groundwater in these two regions compared to other regions, such that they do not yet reflect the short-term nitrogen control measures.

(4). There is a lack of discussion of the pathways of nitrate transport in relation to the sources and also a lack of discussion of nitrate removal processes. Regarding groundwater nitrate source "manure & sewage". It is not clear why manure and sewage are one class. Are these sources similar in terms of isotopic composition? However, the pathways for their transport are totally different.

Re: Thank you for your valuable comments. In response to your concerns, we have added a discussion on the pathways of nitrate transport to the sources, as well as the nitrate removal processes. Regarding the classification of "manure & sewage" as one source, this was based on similarities in their isotopic composition, which can make them difficult to differentiate in certain analyses (See Lines 408-416 and Lines 596-600).

Lines 408-416:

The lower nitrate concentration in deep groundwater may be influenced by multiple factors. DO concentrations decrease with increasing depth (Fig. 6c), thus leading to anoxic conditions that enhance denitrification, which can lower nitrate concentrations in deep groundwater[24]. This is further supported by the significant positive correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (Fig. S7). However, reducing minerals, such as pyrite, can also chemically react with nitrates, contributing to nitrate reduction in deeper groundwater. Further research therefore is needed to fully understand the relative contributions of denitrification and reducing minerals in nitrogen removal from deep groundwater.

Lines 596-600:

The transport pathways of manure and sewage differ, with sewage often reaching groundwater through leaching or leaking pipes and manure typically through agricultural runoff. However, manure and sewage have overlapping isotopic signatures, which make it challenging to differentiate them. We therefore group 'manure & sewage' in one class, as similarly done in literature[41,83].

(5). Sewage when spread on the land can move to groundwater by leaching, while sewage can move to aquifers when sewage pipes are leaking, or when human excreta are used to fertilize the land. However, the latter practice was very important in the 1970's but is not common any longer in China at present.

Re: Thank you for your insightful feedback. We have incorporated this point into the manuscript, discussing how sewage can enter groundwater through leaching when applied to land or due to the leakage of sewage pipes. Additionally, we have included the historical context regarding the use of human excreta as fertilizer, which was common in the 1970s but is no longer a widespread practice in China. This has been clarified and discussed in the revised manuscript (See Lines 218-221).

Lines 218-221:

The unexpectedly dominant presence of manure & sewage in medium groundwater may be linked to irrigation practices from the 1970s, when manure & sewage were commonly used, although these practices are much less common in China today[43].

(6). Also, there is a clear influence of manure and sewage on deep groundwater layers. How is this possible? This needs some more thinking and clarification.

Re: Thank you for your thoughtful suggestion. Based on your feedback, we have re-evaluated the end-member values in this study to ensure that they cover different regions. Our recalculations indicate that soil nitrogen is indeed the largest contributor to the deep groundwater layers. In contrast, manure & sewage had the greatest influence on medium groundwater, which aligns with the sewage irrigation practices from the 1970s. This clarification has been included in the revised manuscript (See Lines 209-227 and **SI** Lines 201-204).

Lines 209-227:

To quantify the contribution of different sources to nitrate, we used a Bayesian stable isotope mixing model (MixSIAR). We considered atmospheric deposition, manure & sewage, soil nitrogen, and chemical fertilizer[41,42] to estimate the potential end-members contributing to nitrate in groundwater (Table S3). The model results showed that nitrate in groundwater primarily originated from soil nitrogen and manure & sewage, accounting for 38.4 ± 23.0% and 31.8 ± 13.4%, respectively (Mean ± SD); atmospheric deposition only contributes a small fraction 10.4 ± 3.3%. The contribution of soil nitrogen is greatest in shallow (44.5 ± 22.9%), deep groundwater (44.1 ± 26.7%), and very deep (40.5 ± 23.3%), whereas manure & sewage dominates the nitrate pool in medium groundwater (44.3 ± 22.1%) (Table S4). The unexpectedly dominant presence of manure & sewage in medium groundwater may be linked to irrigation practices from the 1970s, when manure & sewage were commonly used, although these practices are much less common in China today[43]. The spatial distribution of nitrogen input to subsurface system varies across ecoregions. For example, in North China, groundwater nitrogen often predominantly originates from manure & sewage (65.1%), with soil nitrogen, atmospheric deposition, and chemical fertilizer contributing 18.0%, 9.3%, and 7.6%, respectively[44]. Conversely, in South West, groundwater nitrate is derived more from chemical fertilizer (32%) than soil nitrogen, atmospheric deposition, and manure & sewage that contribute 25%, 18%, and 25%, respectively[45].

SI Lines 201-204:

Table S3. Isotopic composition of four potential NO_3^- end-members used in MixSIAR model.

Sources	$\delta^{15}N\text{-}NO_3^-$		$\delta^{18}O\text{-}NO_3^-$	
	Mean	SD	Mean	SD
Atmospheric Deposition	4.6	3.9	54	13.2
Soil Nitrogen	7.5	5.23	-2.0	8.0
Manure & Sewage	15.0	1.2	-2.0	8.0
Chemical Fertilizer	0.0	1.4	-2.3	0.6

Data obtained from Liu, et al. [4], Ren, et al. [5], Black and Waring [6], Choi, et al. [7], Curt, et al. [8], Ding, et al. [9], Zong, et al. [10], Yu, et al. [11].

(7). Lines 387 and onwards: this is an important observation and also needs more discussion. When denitrification is an important process, there needs to be nitrate (or other forms) and carbon forms or inorganic electron donors including reduced manganese (Mn^{2+}), ferrous iron (Fe^{2+}) and sulfides. Pyrite is the most common iron disulfide mineral in rock. It is found most often in metamorphic and sedimentary rocks where it occurs as either a primary mineral or a fine, widespread impregnation of subsequent origin. Pyrite is frequently found in association with coal and shale deposits. It is therefore interesting to analyze this further. In the data for the random forest model, one of the factors is the lithology. I was wondering if there is a relationship between nitrate concentrations and the lithology. It may not appear as a significant factor due to the method used, but if analyzed differently, it may come out as an important factor explaining nitrate removal.

Re: Thank you for your valuable comment. We apologize that our results do not clarify this point. In this study, the random forest model data did not include lithology as a factor. However, we further demonstrated denitrification using nitrate isotope data (Fig. S6), and we have now added a discussion on the potential impact of lithology on nitrate removal processes in the revised version of the manuscript (See Lines 409-416 and **SI** Lines 135-142).

Lines 409-416:

DO concentrations decrease with increasing depth (Fig. 6c), thus leading to anoxic conditions that enhance denitrification, which can lower nitrate concentrations in deep groundwater[24]. This is further supported by the significant positive correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ (Fig. S7). However, reducing minerals, such as pyrite, can also chemically react with nitrates, contributing to nitrate reduction in deeper groundwater. Further research therefore is needed to fully understand the relative contributions of denitrification and reducing minerals in nitrogen removal from deep groundwater.

SI Lines 135-142:

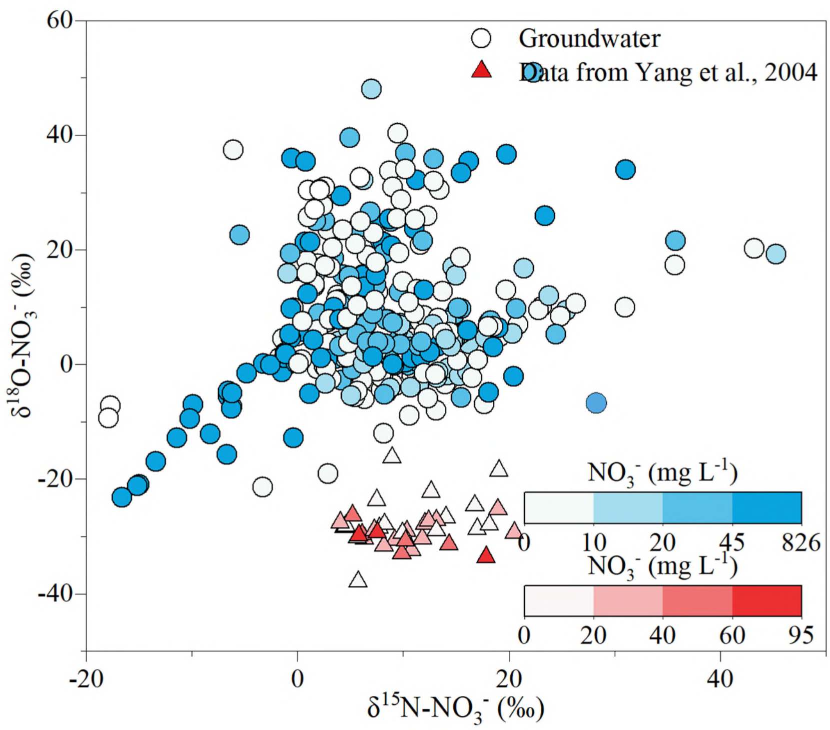

Fig. S7 The relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values in Chinese groundwater. Apart from the study by Yang, et al. [1], there is a clear positive correlation between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values in Chinese groundwater, indicating that denitrification plays a significant role in this context. Meanwhile, Yang, et al. [1] also noted that the region is substantially influenced by denitrification. Therefore, it can be concluded that nitrogen removal in Chinese groundwater is primarily controlled by denitrification processes.

(8). Lines 318-319: "abundant rainfall throughout the year facilitates the leaching of legacy nitrogen and the utilization of nitrogen fertilizer". How can abundant rainfall facilitate fertilizer use? Many regions with a (seasonal) rainfall deficit have irrigation, so I do not understand why only rainfall is important and irrigation has been ignored. For example, irrigation is important in the North China Plain.

Re: Thank you very much for your helpful suggestion. We apologize for the confusion caused by the previous wording. Irrigation plays a crucial role, especially in regions like the North China Plain, where there is a seasonal rainfall deficit. We have now reorganized and revised this section to better reflect the role of both rainfall and irrigation in facilitating nitrogen fertilizer utilization (See Lines 318-328).

Lines 318-328:

The observed isotopic enrichment of $\delta^{18}O\text{-}NO_3^-$ in NC with deeper groundwater likely arise from more evaporation[13]. In contrast, this does not occur as much in the humid SW[57]. In effect, low precipitation in NC probably reduce transport and nitrogen use efficiency[28,44]. In contrast, in wet and rainy SW, abundant rainfall throughout the year facilitates the leaching of legacy nitrogen, as well as the utilization of nitrogen fertilizers through more sufficient soil mositure[58,59]. Although widespread irrigation practices are present in NC, they are primarily concentrated during the crop growing seasons[60]. For much of the year, soil moisture remains relatively low, limiting the transformation and mobility of soil nitrogen. This intermittent moisture availability may further restrict soil nitrogen transport and processing, contributing to lower nitrogen use efficiency outside the irrigation periods[59].

(9). The paper needs thorough editing, for example "Although there has been an overall improvement in groundwater nitrogen pollution in China since 2016" suggests that the pollution has been improved, but I guess the authors mean that pollution has been reduced or the groundwater quality has been improved.

Re: Thank you very much for your suggestion. We have clarified these statements (See Lines 34-35 and Lines 365-367) and edited them carefully throughout the manuscript.

Lines 34-35:

Although there has been an overall decline in groundwater nitrogen pollution in China since 2016, persistent pollution lingers.

Lines 365-367:

Notably, overall groundwater nitrogen pollution significantly declined during 2016–2020 compared with the data from 2000 to 2015, except in the NC and MYR (Fig. 5a).

(10). Other examples: What is the difference between aquifer depth and groundwater table.

Re: Thank you very much for your suggestion. We apologize for this confusion. In this study, 'aquifer depth' refers to the 'groundwater table.' We have clarified this in the manuscript to avoid further misunderstandings (See Lines 78-81).

Lines 78-81:

previous studies have shown that groundwater table can serve as a representative measure of local aquifer depth in numerous regions[30,31]. Therefore, it is reasonable and innovative to study the role of aquifer depth on nitrate dynamics by utilizing data from wells.

(11). Lines 134-135: higher than what?

Re: Thank you very much for your suggestion. We have revised this (See Lines 131-133).

Lines 131-133:

In addition, lowlands with dense population displayed higher average nitrate concentration (36.1 ± 76.7 mg L^{-1}) compared to the middlelands and highlands.

(12). Line 203: sentence not correct?

Re: Thank you very much for your suggestion, and we have revised it (See Lines 197-200).

Lines 197-200:

Although the majority of samples fell within the theoretical range of nitrification (as indicated by the box regions in Fig. S3a-d), some were outside this range, suggesting that the potential role of other processes such as denitrification in regulating nitrate concentrations[39].

(13). Line 187: drivers?

Re: Thank you very much for your suggestion. We have revised this (See Lines 181-183).

Lines 181-183:

These changes in nitrate dynamics and isotopes indicated combined influence of multiple drivers, which will be discussed in the subsequent section.

(14). Line 253: “drinking standard” should be “excellent water quality”. The WHO standard for drinking water is 50 mg nitrate per liter.

Re: Thank you very much for your suggestion. We have revised this (See Lines 255-256).

Lines 255-256:

However, only less than half of the groundwater (44.8%) meets the water quality standard of 10 mg L^{-1} (Fig. S4).

(15). Line 264: this further confirmed ….; why is that a confirmation?

Re: Thank you very much for your suggestion. We have revised this (See Lines 266-269).

Lines 266-269:

This indicated that anthropogenic activities have impacted depths up to ca. 140 m (i.e., Class I groundwater), and denitrification has concurrently affected shallow groundwater (≤ 8 m) due to abundant carbon sources[51].

Minor comments

(16). Just before Line 78: how can the thickness (depth) of aquifers be inferred from wells or hand-dug holes?

Response: Thank you for this comment. In this study, the aquifer depth data we collected came from groundwater table measurements provided in the referenced studies (See Lines 78-81 and supplement data).

Lines 78-81:

previous studies have shown that groundwater table can serve as a representative measure of local aquifer depth in numerous regions[30,31]. Therefore, it is reasonable and innovative to study the role of aquifer depth on nitrate dynamics by utilizing data from wells.

(17). Lines 78-80: I think data from wells have been used elsewhere.

Response: Thank you for this comment. The data from wells were derived from available published papers since 2000, and we have provided all relevant references in the supplementary data. To provide a comprehensive analysis, we ensured that the dataset encompassed essential gradients of geographical, climatic, and human factors. Additionally, the data were examined from multiple perspectives to capture different aspects of groundwater dynamics.

(18). Line 125: what is the first number between brackets, is it the average?

Re: Thank you for your question, and we apologize for not providing a clearer notation. The first number in brackets represents the mean ± SD (See Lines 121-124).

Lines 121-124:

Nitrate concentrations (Unless otherwise specified, represents NO_3^- rather than N-NO_3^- in this study) ranged from 0 to 824.6 mg L^{-1} (31.2 ± 69.4 mg L^{-1} (Mean ± SD); median: 9.0 mg L^{-1}), exceeding previous reports by Gu, et al. [9] (10.9 ± 18.1 mg L^{-1} in groundwater in China) and Ioannis, et al. [13] (5.5 ± 5.1 mg L^{-1} in global groundwater).

(19). Line 142: do you mean groundwater aquifers under croplands?

Re: Yes, thank you very much for your suggestion. We have revised this (See Lines 138-140).

Lines 138-140:

This is also consistent with nitrate concentrations in rivers, for example, in the United States[33], although mean nitrate concentrations of groundwater aquifers are usually higher under croplands.

(20). Table S1, for the soils data it is not clear what exactly has been used, what is the resolution, what soil depth or layer, etc etc; for the climate data: spatial resolution used?

Re: Thank you very much for your suggestion. We have revised it (see **SI** Lines 198-199).

SI Lines 198-199:

Table S2. Global spatially continuous environmental variables considered in the analysis and prediction of nitrate concentrations in groundwater (At the equator, 30” is approximately equal to 1 km; “−” represents no unit).

Type	Short name	Full name	Unit	Resolution	Reference
Climate	AI	Aridity Index	−	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Climate	ET	Potential Evapotranspiration	mm	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Climate	ETsd	Potential Evapotranspiration sd	mm	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Climate	MAP	Precipitation	mm	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	SR	Solar Radiation	kJ m^{-2} day^{-1}	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	MAT	Temperature Mean	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	TMAX	Temperature Max	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	TMIN	Temperature Min	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	VAPOR	Water vapor pressure	kPa	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	BIO1	Annual Mean Temperature	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO2	Mean Diurnal Range	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO3	Isothermality	°C	30' × 30'	https://worldclim.org/data/bioclim.html

Climate	BIO4	Temperature Seasonality	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO5	Max Temperature of Warmest Month	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO6	Min Temperature of Coldest Month	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO7	Temperature Annual Range	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO8	Mean Temperature of Wettest Quarter	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO9	Mean Temperature of Driest Quarter	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO10	Mean Temperature of Warmest Quarter	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO11	Mean Temperature of Coldest Quarter	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO12	Annual Precipitation	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO13	Precipitation of Wettest Month	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO14	Precipitation of Driest Month	mm	30' × 30'	https://worldclim.org/data/bioclim.html

Climate	BIO15	Precipitation Seasonality (Coefficient of Variation)	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO16	Precipitation of Wettest Quarter	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO17	Precipitation of Driest Quarter	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO18	Precipitation of Warmest Quarter	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO19	Precipitation of Coldest Quarter	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	WS	Wind Speed	$m\ s^{-1}$	30' × 30'	https://worldclim.org/data/worldclim21.html
Human activities	PD	Population Density	People km^{-2}	1 km × 1 km	https://landscan.ornl.gov/
Soil	BDOD	Bulk Density (0 ~ 200 cm)	kg dm^{-3}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	CEC	Cation Exchange Capacity (0 ~ 200 cm)	cmol kg^{-1}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	CFVO	Volumetric Fraction of Coarse Fragments (0 ~ 200 cm)	volume %	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	CLAY	Clay Content	%	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	HYSOGs	Global Hydrologic Soil Groups (0 ~ 200 cm)	–	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1566

Soil	TSN	Total Soil Nitrogen (0 ~ 200 cm)	g kg^{-1}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	OCD	Organic Carbon Density (0 ~ 200 cm)	hg dm^{-3}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	OCS	Organic Carbon Stocks (0 ~ 200 cm)	kg m^{-2}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	PH	Soil pH (0 ~ 200 cm)	–	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	SAND	Sand Content (0 ~ 200 cm)	%	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	SILT	Silt Content (0 ~ 200 cm)	%	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	SOC	Soil Content Carbon (0 ~ 200 cm)	g kg^{-1}	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Soil	VWC	Volumetric Water Content (0 ~ 200 cm)	%	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	SSDT	Average Soil and Sedimentary-deposit Thickness	m	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	Curvature	Curvature	–	250 m × 250 m	https://zenodo.org/records/1447210

Topography	DC	Downlslope Curvature	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	DVM	DVM2	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	Landform	Landform	–	250 m × 250 m	https://zenodo.org/records/1464846#.YoXUVOhBw2w
Topography	Lithology	Lithology	–	250 m × 250 m	https://zenodo.org/records/1464846#.YoXUVOhBw2w
Topography	MRN	MRN	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	NEG	NEG	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	POS	POS	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	Slope	Slope	°	250 m × 250 m	https://zenodo.org/records/1447210

Topography	TPI	Topographic Position Index	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	TWI	Topographic Wetness Index	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	UPCUR	Upslope Curvature	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	VBF	Valley Bottom Flatness	–	250 m × 250 m	https://zenodo.org/records/1447210
Topography	Elevation	Elevation	m	30' × 30'	https://worldclim.org/data/worldclim21.html
Topography	GRR	Groundwater Recharge Rate	m $year^{-1}$	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01621-x
Topography	HSVB	Hill-slope Valley-bottom	–	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	LC	Land Cover Mask	–	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	UVB	Upland Valley-bottom and Lowland Sedimentary Deposit Thickness	m	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	WDR	Groundwater depletion rate	mm yr^{-1}	0.05° × 0.05°	https://doi.org/10.1038/ngeo1617

Topography	UHSRT	Upland Hill-slope Regolith Thickness	m	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	UHSST	Upland Hill-slope Soil Thickness	m	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Vegetation	GPP	Gross Primary Productivity	kg C m^{-2} $year^{-1}$	1 km × 1 km	https://developers.google.com/earth-engine/datasets/catalog/MODIS_061_MOD17A3HGF
Vegetation	LAI	Leaf Area Index	–	0.08° × 0.08°	https://www.resdc.cn/data.aspx?DATAID=336
Vegetation	LUT	Land Use Types	–	0.05° × 0.05°	https://data.casearth.cn/sdo/detail/6123651428a58f70c2a51e49

21. Line 478: "To minimize the direct influence of external inputs and focus on the groundwater biogeochemical processes of nitrogen, this study excluded individual significant outliers (i.e., nitrate concentration ≥1000 mg L-1)." Totally unclear why the high values are excluded.

Re: Thank you very much for your suggestion. We apologize for the confusion caused by our description. We have revised this section to provide a clearer explanation of how outliers were excluded from the analysis (See Lines 499-502).

Lines 499-502:

To ensure the reliability of data, significant outliers (below the first quartile minus 1.5 × interquartile range (IQR) or above the third quartile plus 1.5 × IQR) were excluded during the process of data processing[80].

Reply to Reviewer #2's major comments:

Reviewer #2 (Remarks to the Author):

Liu 2024 Nature - Chronic nitrogen legacy in the aquifers of China

This manuscript is generally well-written. However, I had concerns with sample collection methods, quality assurance, and consistency and integrity of the data as detailed below.

Thanks for your constructive comments and suggestions, which have helped us to thoroughly revise and improve the manuscript. Please find our responses to your comments, which we have incorporated in the revised manuscript.

(1). **PL6** (The previous line (**PL**) number from the abstract in the initial submission): How were the GW sites identified and chosen and how did authors ensure that they covered the "gradients of geographical, climate, and human factors"?

Re: Thank you for your comment. We have provided a more detailed explanation of how the groundwater sites were identified and selected, ensuring that they cover the gradients of geographical, climatic, and human factors. This clarification has now been included in the revised manuscript (See Lines 502-506).

Lines 502-506:

To ensure the dataset covers the gradients of geographical, climatic, and human factors, we incorporated data from regions with diverse elevations, distinct climate zones, varied land use types, and population densities. This allowed us to capture the wide-ranging groundwater conditions, facilitating a thorough analysis of spatial and environmental variability.

(2). **PL14**: were GW wells measured in 2016 and more recently? Were they measured once and how was variability in N quantified?

Re: Thank you for your insightful comment. In this study, we summarized the groundwater nitrate concentration data for different economic regions over two periods: 2000-2015 and 2016-2020. This allowed for a comprehensive comparison of the variability in nitrogen levels over time (see ***Supplementary Information*** **(SI)** Lines

207-208).

SI Lines 207-208:

Table S5. Number of samples in different economic zones from 2000 to 2020 (N = 3163). Note: Some groundwater sampling sites do not directly provide the sampling time.

Year	NC	MYR	NE	SW	EC	NW	MCY	SC
	Number							
2000	24	37						
2001	28	18				28		
2002				52	18			
2003		16	10			10		32
2004	13	1	43					15
2005	12							
2006				25		40		23
2007				25		40		
2008	32	37		20		4		
2009	23	49		37		59		
2010	22		43		21	82	5	120
2011	54		137			135		
2012	29			41				
2013			4	26	28	13		31
2014	58	22				203		39
2015	179					17		64
2016	3			29		184		24
2017	58	23		1			13	
2018		24	9	23		38	29	
2019	42	254		22	41	44	7	
2020		50		11			90	

(3). **PL47**: maybe change “is essential” to “facilitates”

Re: Thank you very much for your suggestion. We have revised this (See Lines 67-68).

Lines 67-68:

Groundwater stores large quantities of nitrogen and facilitates nitrogen transport, transformation, and accumulation[27-29].

(4). **PL58**: suggest period after China

Re: Thank you very much for your suggestion. We have revised this (See Lines 76-78).

Lines 76-78:

The main reasons for this are as follows: natural convenience for groundwater sampling; moreover, groundwater nitrate dynamics have been extensively investigated throughout China since 2000.

(5). **PL59:** readers may not understand “hand-dug aquifer depth”

Re: Thank you very much for your suggestion. We have changed the “hand-dug aquifer depth” to “groundwater table” (See Lines 78-80).

Lines 78-80:

additionally, previous studies have shown that groundwater table can serve as a representative measure of local aquifer depth in numerous regions[30,31].

(6). **PL62**: water may be pumped from the top or the bottom of an aquifer, so hand dug depth may not reveal GW table. Also, GW table can fluctuate especially in regions where GW is pumped for ag at rates higher than recharge.

Re: Thank you very much for your insightful comment. In this study, we collected groundwater table data from the literature, which reflect the measurements provided in those sources (see supplementary data).

(7). **PL65**: suggest deleting “to the best of our knowledge”. We assume this is the case.

Re: Thank you very much for your suggestion. We have deleted it.

(8). **PL78**: is this the proper order? Why are methods last?

Re: Thank you for your thoughtful comment. According to the journal's guidelines, the Methods section must be placed at the end of the manuscript.

(9). Figure 1: I’m confused by the legends of the figures. Where do the legends end and the main text begin? It seems that the authors have a very long legend for the figures in which they are discussing site selection, characterization, and sampling approach. I suggest that these descriptions be placed with the methods section. For example, the study site description is embedded in the figures. I find this approach of organization confusing and does not seem standard. Suggest that the tables and figures with their respective legends be placed at the end of manuscript.

Re: Thank you for your valuable feedback. We appreciate your suggestion regarding the organization of the figures and their legends. We have revised the manuscript to separate the figure legends from the main text more clearly and moved the detailed descriptions of site selection, characterization, and sampling approaches to the Methods section. Additionally, we have placed the tables and figures with their respective legends at the end of the manuscript, as you have suggested (See Lines 105-120 and Lines 547-557).

Lines 105-120:

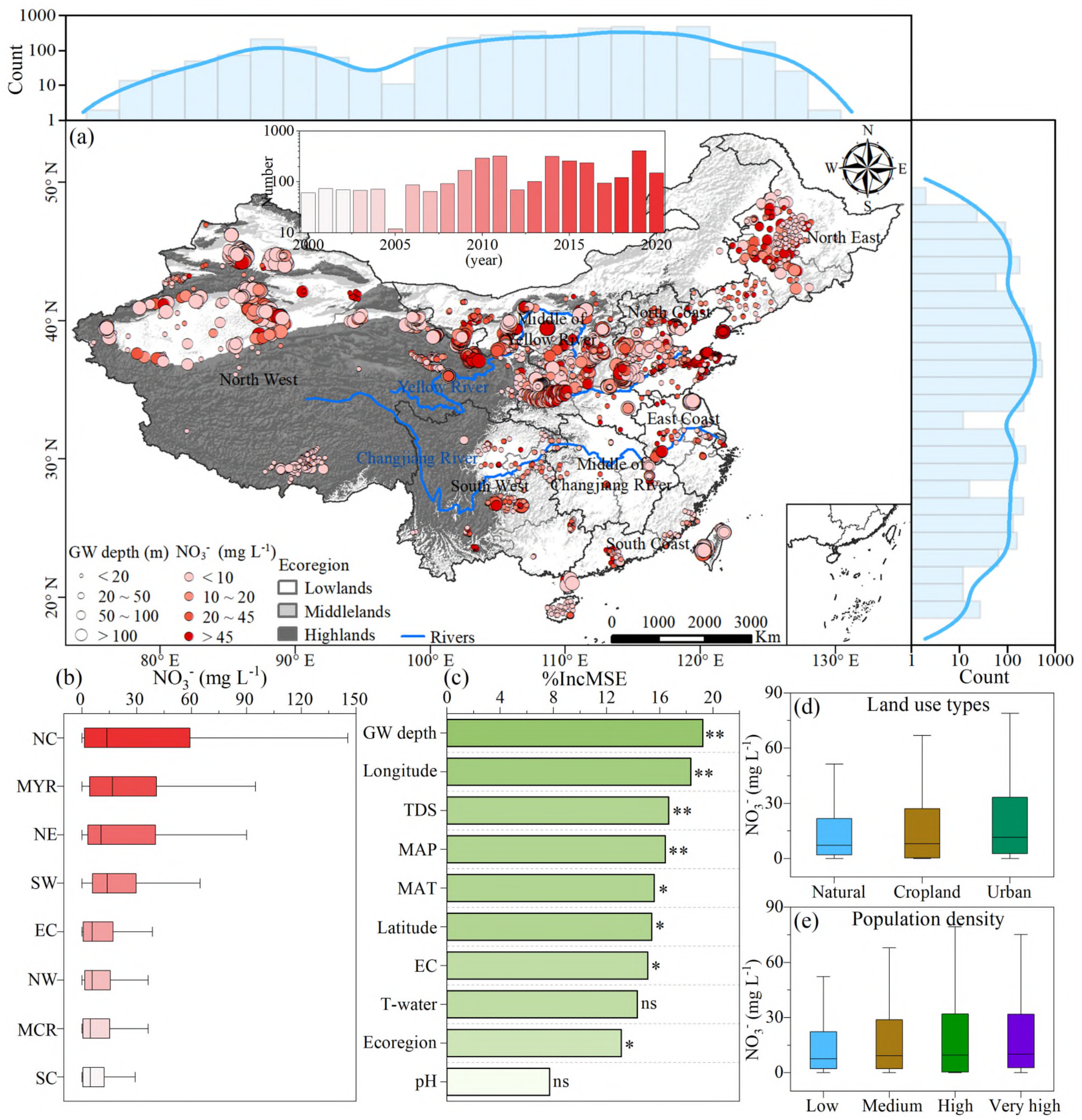

Fig. 1 The spatial variation of nitrate concentrations in 4,047 groundwater sites in China. (a) The upper and right subgraphs show the counts of the longitude and latitude distributions of the sample sites, respectively. The red bar chart above the map shows the number of sampling points in different years. (b) Mean concentrations of nitrate in eight economic regions, namely North Coast (NC), Middle of Yellow River (MYR), North East (NE), South West (SW), East Coast (EC), North West (NW), Middle of Changjiang River (MCR), and South Coast (SC). (c) The relative importance of influential drivers for groundwater nitrate concentrations was determined by regression forecasting using random forests. The columns marked * ($P < 0.05$) and ** ($P < 0.01$) represent drivers have significant impacts on nitrate concentrations, while ns ($P > 0.05$) indicate that drivers have no significant differences on nitrate dynamics. (d) and (e)

Nitrate concentrations under different land use types and population density, respectively (classification methods in Materials and Methods). The box plots include three modules, box limits, upper and lower quartiles; small cube, average value; center line, and median.

Lines 547-557:

RF model has been frequently applied in the field of environmental science to map the nitrate distribution and identify key influencing factors and control mechanisms. In this study, 68 spatially continuous environmental variables that may be directly or indirectly related to nitrate accumulation in groundwater were combined as potential predictors (Table S2). The principle of prediction uncertainty was calculated by the Bootstrap method by generating different Bootstrap samples, this study obtains various models. The differences in predictions from these models capture the uncertainty inherent in the modeling process. This method effectively quantifies how variations in the input data can lead to variations in the model outputs, thus reflecting the uncertainty in the predictions.

(10). How were GW wells sampled? In what way were the data checked for consistency? In what way were the data checked for accuracy?

Re: Thank you for your insightful comment. The groundwater wells sampled in this study were sourced from publicly available data. To ensure data quality, we employed standard methods to identify and assess outliers in the dataset. This approach helped maintain consistency and accuracy in our analysis (See Lines 498-501).

Lines 499-502:

To ensure the reliability of data, significant outliers (below the first quartile minus 1.5 × interquartile range (IQR) or above the third quartile plus 1.5 × IQR) were excluded during the process of data processing[80].

(11). **PL79**: change to “at” to “in”

Re: Thank you for your comment. We have revised it (See Line 98).

Lines 98:

The dynamics of nitrate concentrations in groundwater across China.

(13). **PL106**: delete "it"

Re: Thank you very much for your suggestion. We have deleted it (See Lines 121-124).

Lines 121-124:

Nitrate concentrations (Unless otherwise specified, represents NO_3^- rather than N-NO_3^- in this study) ranged from 0 to 824.6 mg L^{-1} (31.2 ± 69.4 mg L^{-1} (Mean ± SD); median: 9.0 mg L^{-1}), exceeding previous reports by Gu, et al. [9] (10.9 ± 18.1 mg L^{-1} in groundwater in China) and Ioannis, et al. [13] (5.5 ± 5.1 mg L^{-1} in global groundwater).

(14). **PL110**: wow, that's high! Is there NH_4 data from any of these samples?

Re: Thank you for your insightful comment. We verified the data, which reflects the values presented. The sources of these data are included in the supplementary data. However, the data we used focused exclusively on NO_3^- concentrations and did not include NH_4^+. We may consider addressing this limitation in future studies.

(15). **PL127**: this description of machine learning and random forest models should be discussed in the methods section and not in the legend to Fig 2.

Re: Thank you for your helpful suggestion. We have revised the manuscript to move the description of machine learning and random forest models from **Fig. 2** legend to the Methods section, as you recommended (See Lines 159-164 and Lines 547-557).

Lines 159-164:

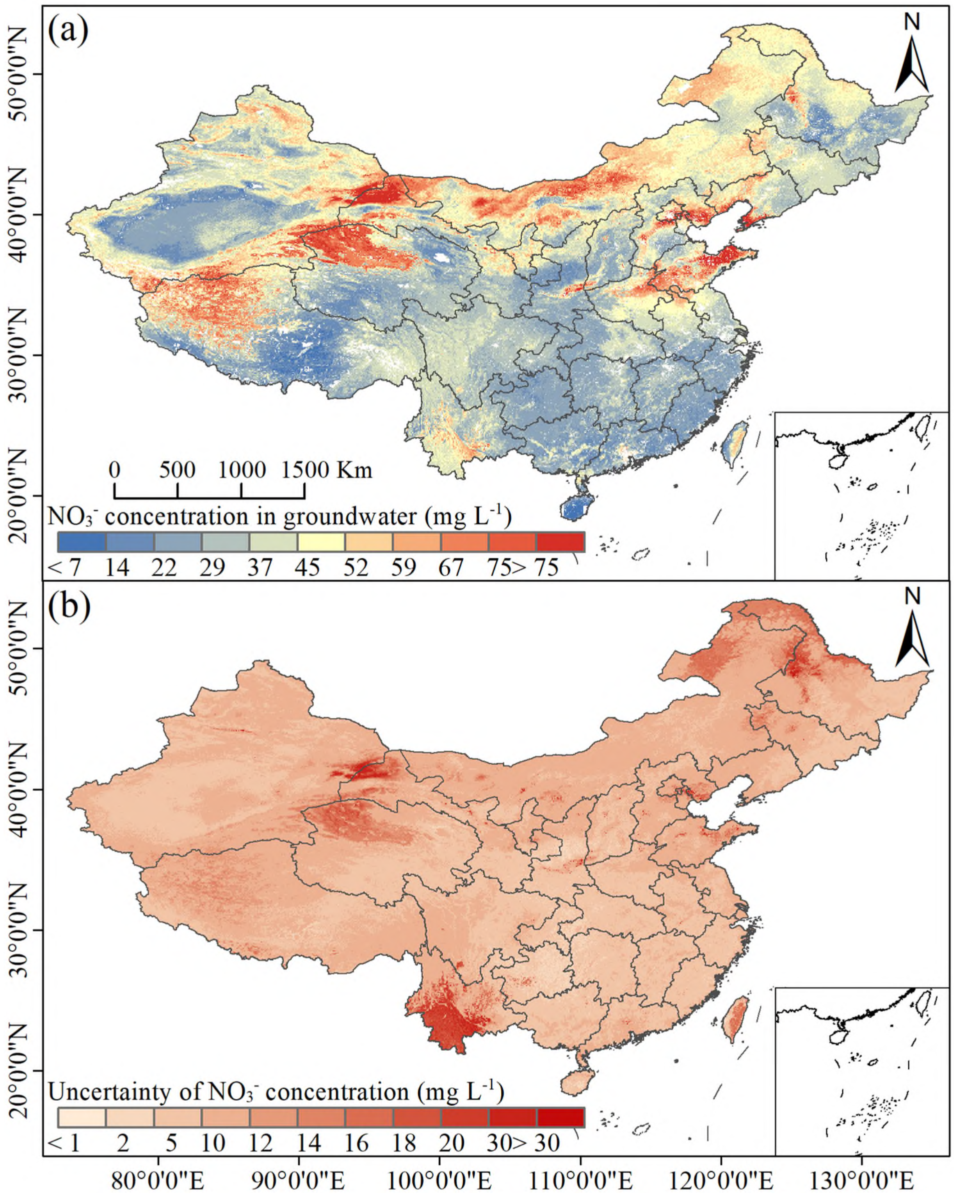

Fig. 2 (a) Simulated nitrate concentrations and (b) uncertainty in the Chinese groundwater by a machine learning algorithm (random forest modeling), which predicted by 68 spatially continuous environmental variables (Table S2). The nitrate values were grouped into 11 categories to generate a color gradient (in the right), where blue and red colors represent low and high values, respectively.

Lines 547-557:

RF model has been frequently applied in the field of environmental science to map the nitrate distribution and identify key influencing factors and control mechanisms. In this study, 68 spatially continuous environmental variables that may be directly or indirectly related to nitrate accumulation in groundwater were combined as potential predictors

(Table S2). The principle of prediction uncertainty was calculated by the Bootstrap method by generating different Bootstrap samples, this study obtains various models. The differences in predictions from these models capture the uncertainty inherent in the modeling process. This method effectively quantifies how variations in the input data can lead to variations in the model outputs, thus reflecting the uncertainty in the predictions.

(16). **PL161**: I wouldn't call aquifer depth a driver because that term implies a mechanism of action. Rather, nitrate concentration correlates with depth due to infiltration and/or or mechanisms of nitrate uptake, e.g. denitrification.

Re: Thank you very much for your suggestion. We have revised this (See Lines 168-170).

Lines 168-170:

Among all hydrochemical characteristics and other influencing factors, aquifer depth exerts the most predominant influence on nitrate concentration in groundwater (Fig. 1c and Fig. 3a-e).

(17). **PL166**: explain what the isotope values indicate. That is, what does a low or high value of O or N mean in this context?

Re: Thank you for your thoughtful feedback. We have revised the manuscript to provide a clearer explanation of the isotope values of oxygen and nitrogen in this context. Additionally, we have provided all relevant references in the supplementary data (See Lines 173-183 and supplement data).

Lines 173-183:

The $\delta^{15}N\text{-}NO_3^-$ increased and then decreased with increasing aquifer depth, peaking at about 8 m (Fig. 3d), suggesting nitrate may have undergone two distinct biogeochemical stages. The first is that more anoxic conditions coupled with increasing carbon sources (e.g., DOC) (Fig. S2a), resulting more denitrification over depth. The subsequent decline may be attributed to declining microbial abundance and carbon and nitrogen sources with increasing aquifer depth[37]. Values of $\delta^{18}O\text{-}NO_3^-$ continued to increase however also show minimum values at peak values of $\delta^{15}N\text{-}NO_3^-$ (Fig. 3e), which may be attributed to processes including water evaporation, which enriched

$\delta^{18}O_{water}$ and subsequent isotopic fractionation during nitrification[13]. These changes in nitrate dynamics and isotopes indicated combined influence of multiple drivers, which will be discussed in the subsequent section.

(18). Do you really have isotope value for all 4000 wells? That would be difficult to accomplish. Please indicate the sample sizes associated with the isotope data across ecoregions.

Re: Thank you for your valuable comment. Isotope data were not available for any of the 4,000 wells. We have revised the manuscript to include the sample sizes associated with isotope data across different ecoregions (see **SI** Lines 210-211).

SI Line 210-211:

Table S6. Numbers and proportion of samples in different categories of groundwater depths, location, ecoregions, land use types, and population density.

Categories	Indicators	Groundwater depth				Location							
		Shallow	Medium	Deep	Very deep	NC	MYR	NE	SW	EC	NW	MCR	SC
NO_3^-	N	709	448	359	657	833	795	313	389	219	985	155	358
	Proportion	32.6%	20.6%	16.5%	30.2%	20.6%	19.6%	7.7%	9.6%	5.4%	24.3%	3.8%	8.8%
$\delta^{15}N$-NO_3	N	402	36	30	49	154	86	8	106	46	30	36	59
	Proportion	77.8%	7.0%	5.8%	9.5%	29.3%	16.4%	1.5%	20.2%	8.8%	5.7%	6.9%	11.2%
$\delta^{18}O$-NO_3	N	313	27	13	40	115	39	8	106	28	10	36	59
	Proportion	79.6%	6.9%	3.3%	10.2%	28.7%	9.7%	2.0%	26.4%	7.0%	2.5%	9.0%	14.7%

Categories	Indicators	Ecoregion			Land use			Population density			
		Lowlands	Middlelands	Highlands	Natural	Cropland	Urban	Low	Medium	High	Very high
NO_3^-	N	2421	1053	565	1372	1727	930	983	1002	997	1057
	Proportion	59.8%	26.0%	14.0%	34.1%	42.9%	23.1%	24.3%	24.8%	24.7%	26.2%
$\delta^{15}N$-NO_3	N	384	96	37	101	259	156	21	223	70	203
	Proportion	74.3%	18.6%	7.2%	19.6%	50.2%	30.2%	4.1%	43.1%	13.5%	39.3%

$\delta^{18}O-NO_3$	N	280	78	35		98	204	90	19	214	45	115
	Proportion	71.2%	19.8%	8.9%		25.0%	52.0%	23.0%	4.8%	54.5%	11.5%	29.3%

(19). **PL170** Fig 3. Why make a bar graph here instead of a continuous biplot of depth vs nitrate concentration? The categories are not indicative of anything and are contrived.

Re: Thank you for your insightful feedback. We used the bar graph in Fig. 3a to examine the overall distribution of nitrate concentrations at different groundwater depths. However, based on your suggestion, we have added a continuous biplot of depth versus nitrate concentration in Fig. 3c to provide a more detailed representation (See Lines 184-192).

Lines 184-192:

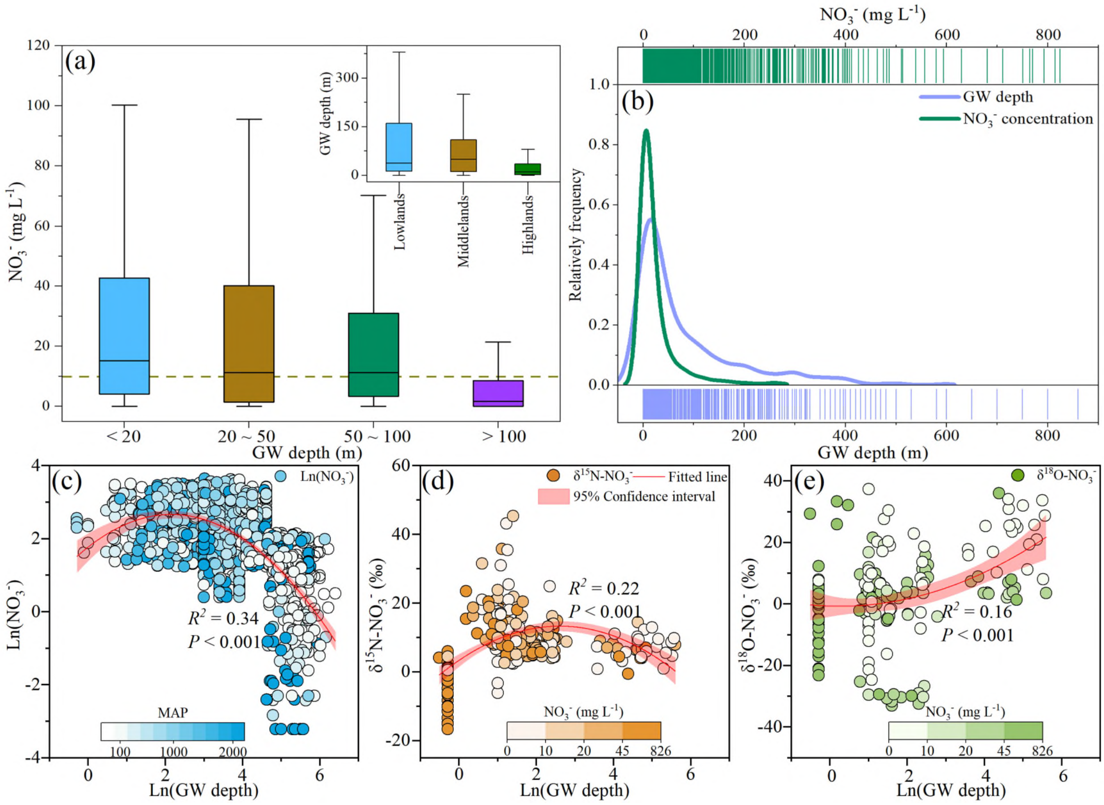

Fig. 3 Nitrate concentrations, isotopes, and groundwater aquifer depth. (a) Nitrate concentrations at various aquifer depths and elevations. (b) The frequency distribution of NO_3^- concentrations and aquifer depths. (c) NO_3^- concentrations, including only samples at the first to third quartile nitrate concentrations for the four classes of aquifer depths, (d) $\delta^{15}N-NO_3^-$, (e) $\delta^{18}O-NO_3^-$ as a function of aquifer depth. Nitrate concentrations generally decrease with increasing depth and MAP (c); values of $\delta^{15}N-NO_3^-$ peak, whereas those of $\delta^{18}O-NO_3^-$ reach lowest values at some intermediate depths (d)-(e).

(20). **PL169**: change drives to drivers

Re: Thank you very much for your suggestion. We have revised this (See Lines 181-183).

Lines 181-183:

These changes in nitrate dynamics and isotopes indicated combined influence of multiple drivers, which will be discussed in the subsequent section.

(22). **PL215**: did the authors try to age date the gw for example, with CFCs, radioisotopes or other methods (e.g. Scott Phillips at USGS has done so with gw in the Chesapeake Bay region of the US).

Re: Thank you for your thoughtful suggestion. Groundwater data were collected from the published literature. Unfortunately, most of these studies did not include groundwater age dating using methods, such as CFCs or radioisotopes. We appreciate your feedback and acknowledge the value of such analyses, which we hope can be incorporated into future research.

(23). **PL232**: poor gw at 0-18m suggests more recent inputs of N

Re: Thank you very much for your suggestion. We have revised it (See Lines 249-252).

Lines 249-252:

It should be noted that in middlelands with both very high and low populations, the groundwater quality deteriorates significantly to a poor level (35%) when aquifer depth ranges from 0 to 18 m (Fig. 4a), which may be attributed to more recent nitrogen inputs[9].

(24). **PL233**: still very confused about the differences among low, middle, highlands. What is important about these regions and why should the drivers be different among these 3 regions? Can the authors show land use characteristics (percentages) among these regions?

Re: Thank you for your suggestions. We have revised the manuscript to better explain the distinctions among lowlands, middlelands, and highlands, the significance of these differences for nitrate dynamics, and added the land use percentage of groundwater samples from different ecoregions (See Lines 516-529).

Lines 516-529:

The classification of ecoregions is based on distinct ecological, climatic, and topographical characteristics, and elevation ranges, which is defined by the Environmental Protection Agency of United States[81,82], respectively. (Table S6 and Fig. 1a). Lowlands (elevation ⩽ 500 m) are typically flat with naturally fertile soils and well-developed drainage systems, making them suitable for agricultural activities and urban development (Land use percentage of groundwater samples: natural (15.6%), cropland (51.8%), and urban (32.6%)). Middlelands (500 < elevation ≤ 1500 m) have more moderate slopes and soils, supporting a mix of agriculture, forestry, and urban development but with less intensity compared to lowlands (Land use percentage of groundwater samples: natural (41.8%), cropland (42.0%), and urban (16.2%)). Finally, highlands (elevation > 1500 m) are characterized by steep slopes and poorly developed soils, making them generally unsuitable for agriculture or urbanization (Land use percentage of groundwater samples: natural (75.7%), cropland (17.6%), and urban (6.7%)).

(24). Fig 4a is interesting but doesn't give me a sense of what are the actual land use factors associated with nitrate. This representation is colorful but difficult to interpret and visualize and we don't have the corresponding data to fully understand relationships among these factors.

Re: Thank you for your valuable feedback. As shown in Fig. 4a, we used categorical variables based on different controlling factors (i.e., population density, ecoregions, and land use) to visually demonstrate the relationships between nitrate concentrations and aquifer depth. We understand that the figure might be challenging to interpret; therefore, we have provided further explanations in the text to clarify the patterns. Additionally, to enhance visualization and deepen the analysis, we developed a Sankey diagram based on these categorical variables, which quantitatively illustrated the classification of groundwater types and their connections to land use. We hope this will help to better understand the relationships between these factors and nitrate levels (See Lines 244-271 and **SI** Lines 120-122).

Lines 244-271:

The correlation between aquifer depth, geographical location, and climate may reflect an intrinsic relationship between aquifer depth and nitrate dynamics (Fig. 4). When aquifer depth was greater than 140 m, most groundwater has low nitrate concentrations, while groundwater below than 140 m in lowlands and middlelands with high population density often have medium (7.5%) and poor (8.8%) water quality as measured by nitrate concentrations (Fig. 4a). It should be noted that in middlelands with both very high and low populations, the groundwater quality deteriorates significantly to a poor level (35%) when aquifer depth ranges from 0 to 18 m (Fig. 4a), which may be attributed to more recent nitrogen inputs[9]. According to the threshold of aquifer depth, the Class I groundwater (≤ 140 m, 75.8%) are mainly located in lowlands (53.5%) and middlelands (33.0%), with cropland being the dominant land cover (49.4%). However, only less than half of the groundwater (44.8%) meets the water quality standard of 10 mg L^{-1} (Fig. S4). In contrast, the Class II groundwater (> 140 m, 24.2%) are mainly situated in lowlands (71.0%) and middlelands (22.8%), characterized by high population density levels (55.8%) and urban land cover types (44.0%), and the overall water quality is excellent (82.4%) (Fig. S4). Additionally, the threshold for nitrate dynamics under different influencing factors showed that most Class II groundwater (> 140 m) are classified as excellent, while there is significant variability in the nitrate dynamics of Class I groundwater (≤ 140 m) (Fig. 4a and Fig. S4), highlighting the substantial impact of anthropogenic activities[33]. Note that, there exist two turning points in nitrate dynamics as aquifer depth increases, one of which is the turning point shown in Fig. 3e (aquifer depth ca. 8 m), while the another is the threshold from decision tree-heatmap (Fig. 4a, aquifer depth ca. 140 m). This indicated that anthropogenic activities have impacted depths up to ca. 140 m (i.e., Class I groundwater), and denitrification has concurrently affected shallow groundwater (≤ 8 m) due to abundant carbon sources[51]. This information can provide theoretical support for sustainable future groundwater quality management by explaining why shallow groundwater are more susceptible to higher nitrates levels.

SI Lines 120-122:

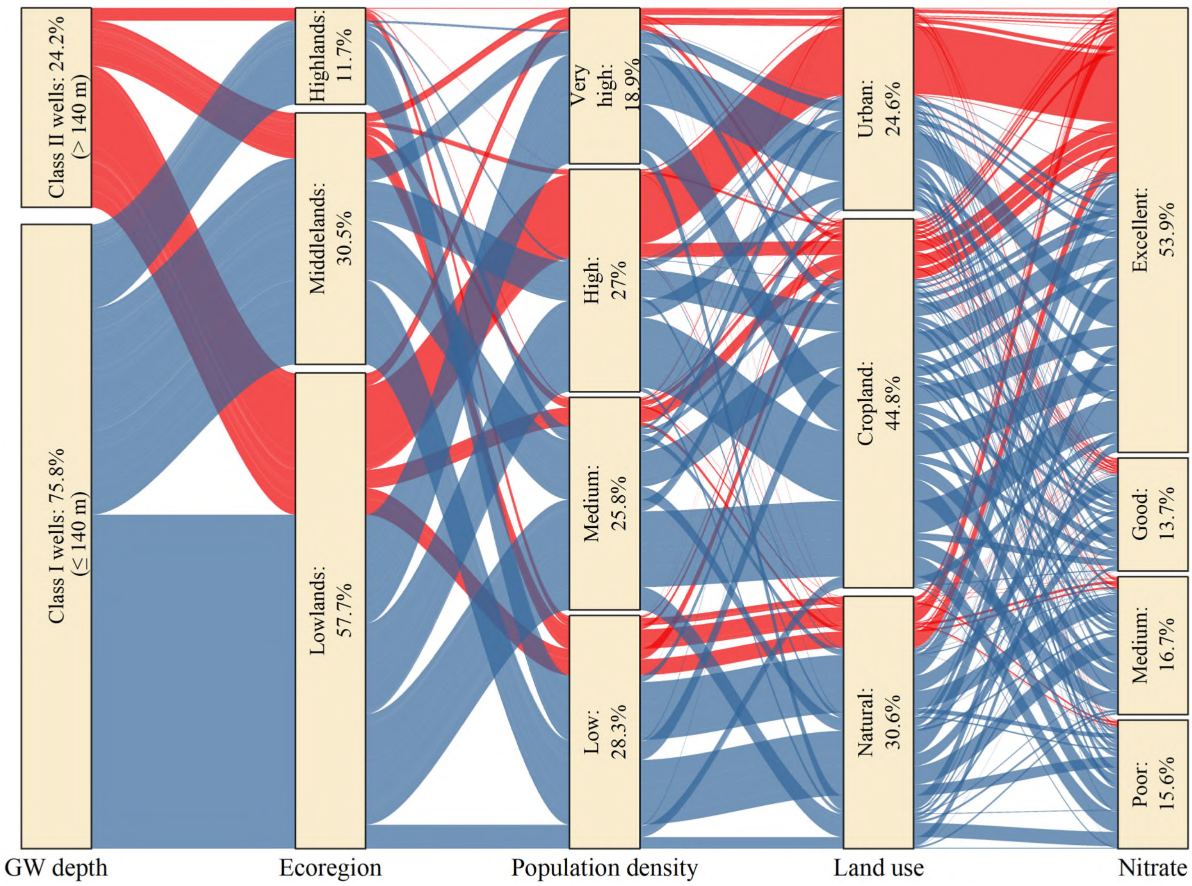

Fig. S4 Sankey diagram displaying the synchronous distribution of class I and II wells in differential ecoregion, population density, land use, and nitrate.

(25). **PL254**: geographic and climate factors have effects on aquifer depth? How so? What does this mean? I can understand how geography and climate affect nitrate but not the depth of the aquifer.

Re: Thank you for your valuable feedback. We appreciate your observation and have reorganized this section to improve clarity. We believe that geographic and climatic factors primarily influence groundwater recharge rates and availability, which in turn affect groundwater levels rather than the depth of the aquifer structure itself. For instance, rainfall plays a critical role in groundwater recharge, directly impacting water table levels, while geological formations and mountainous topography influence the variability in groundwater depth. This study has revised the text to reflect these nuances more clearly, ensuring that the distinction between the factors influencing nitrate dynamics and aquifer properties is appropriately made (See Lines 272-280).

Lines 272-280:

The association among external factors (including geographical and climate factors), aquifer depth, and nitrate concentration using structural equation model, which showed interesting relationships (Fig. 4b-c). TDS (λ = 0.61), EC (λ = 0.44), and geographical factors (λ = 0.26) exhibited positive effects on nitrate, while aquifer depth (λ = -0.15) and T-water (λ = -0.14) shown negative effects. Furthermore, the total effect of climate factors (λ = 0.40) on nitrate is the highest, wherein the indirect effect of aquifer depth (λ = -0.22) and climate factors (λ = 0.46) surpassed the direct effect. However, the direct effect of geographical factors (λ = 0.26) remains greater than both indirect effects combined.

(26). **PL288**: how did redox affect GW in this study? Did the authors collect data on redox?

Re: Thank you for your insightful suggestions. We have reorganized the redox-related data and incorporated a detailed discussion in the manuscript. Specifically, we examined how redox conditions influenced nitrate concentrations and denitrification processes in groundwater (See Lines 175-177, Lines 308-311, and **SI** Lines 113-115).

Lines 175-177:

The first is that more anoxic conditions coupled with increasing carbon sources (e.g., DOC) (Fig. S2a), resulting more denitrification over depth.

Lines 308-311:

Munz, et al. [56] demonstrated that temporal variations in temperature and redox zonation dominate the migration and degradation of nitrate within groundwater aquifer, which is also verified by the relationship between Oxidation-Reduction Potential (Eh) and NO_3^- in this study (Fig. S2b).

SI Lines 112-114:

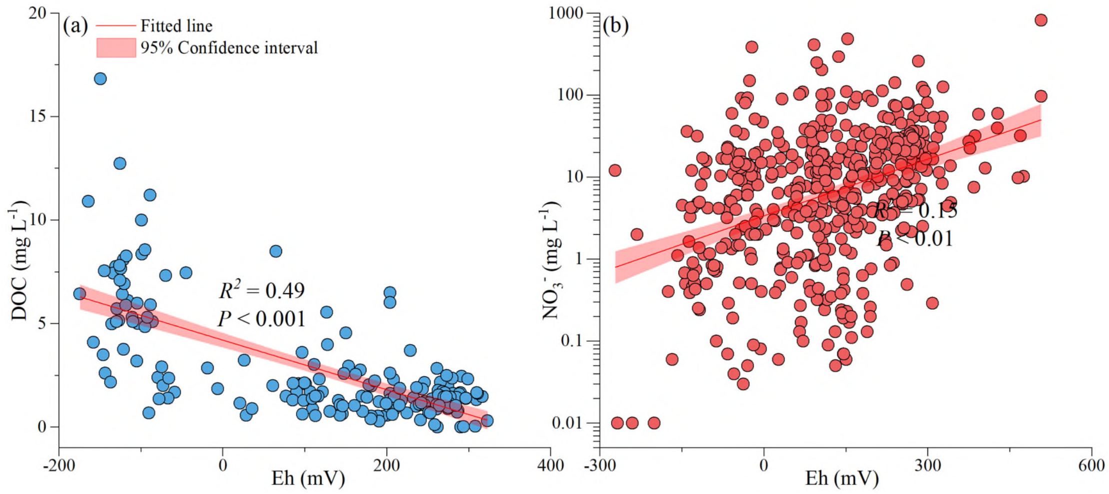

Fig. S2 The relationship between Eh and (a) NO_3^- and (b) DOC values in Chinese groundwater.

(27). **PL333**: how was this time comparison made? No methods are described here. Were the same wells sampled during these time periods. How were they sampled?

Response: Thank you for this comment. In this study, we summarized groundwater nitrate concentration data for different economic regions over two periods: 2000-2015 and 2016-2020, enabling a comprehensive comparison of the variability in nitrogen levels over time (see **SI** Lines 207-208). Data were collected from published papers, which may reflect differences in sampling methods across studies. However, we conducted thorough analyses to ensure the reliability and comparability of the data (See Lines 499-502 and **SI** Lines 207-208).

Lines 499-502:

To ensure the reliability of data, significant outliers (below the first quartile minus 1.5 × interquartile range (IQR) or above the third quartile plus 1.5 × IQR) were excluded during the process of data processing[80].

SI Lines 207-208:

Table S5. Number of samples in different economic zones from 2000 to 2020 (N = 3163). Note: Some groundwater sampling sites do not directly provide the sampling time.

Year	NC	MYR	NE	SW	EC	NW	MCY	SC
	Number							

2000	24	37						
2001	28	18				28		
2002				52	18			
2003		16	10			10		32
2004	13	1	43					15
2005	12							
2006				25		40		23
2007				25		40		
2008	32	37		20		4		
2009	23	49		37		59		
2010	22		43		21	82	5	120
2011	54		137			135		
2012	29			41				
2013			4	26	28	13		31
2014	58	22				203		39
2015	179					17		64
2016	3			29		184		24
2017	58	23		1			13	
2018		24	9	23		38	29	
2019	42	254		22	41	44	7	
2020		50		11			90	

(28). It is speculation to say that they were significant effects due to treatment measures in 2015. What were these treatment measures? How could they have made such a large effect so quickly when previous data shown here demonstrates the chronic effects of legacy nitrogen? What mechanisms could account for such a rapid effect of management actions? No such rapid effect has been demonstrated in other regions/countries with high GW N. On line 429, the authors emphasize the fact that "nitrogen pollution control is a long-term process that does not yield immediate results due to the presence of legacy nitrogen". How then, did the rapid change occur that is depicted in fig 5?

Re: Thank you for your thoughtful comments. We apologize for this confusion. The rapid change depicted in Fig. 5 may have led to some misunderstanding. In 2015, China implemented new groundwater protection policies and divided groundwater nitrate concentrations across different economic regions into two comparison periods, 2000–2015 and 2016–2020. However, as we emphasized on line 429, "nitrogen pollution control is a long-term process that does not yield immediate results due to the presence of legacy nitrogen." The observed improvements between the two periods were not uniform across all regions. Our results indicate that regions with shallower soil layers showed more noticeable improvements in groundwater quality during 2016–2020. In contrast, regions with deeper soil layers, such as the Middle Yellow River (MYR) and the North Coast (NC), exhibited limited improvement. This reflects the complexity of nitrogen transport and the persistence of legacy nitrogen, reinforcing the notion that recovery is gradual and varies depending on the soil depth, land use, and hydrogeological characteristics. We hope that this explanation clarifies the observations in our study (See Lines 357-376).

Lines 357-376:

Statistics indicated a consistent increase in the discharge of TN and ammonia wastewater prior to 2015 (Fig. S6). In response, the Chinese government implemented a series of comprehensive treatment measures in 2015 that effectively mitigated this trend[66], such as improving wastewater treatment. Although the data used in this study are based on single sampling events, the data points across different economic zones are widely distributed between 2000 and 2015 and 2016–2020 (see the numbers of samples in different economic zones from 2000 to 2020 in Fig. 1a and Table S5). To better capture temporal variations, we also calculated the overall means and standard deviations (SD) for the two periods: 2000–2015 and 2016–2020 (Fig. 5). Notably, overall groundwater nitrogen pollution significantly declined during 2016–2020 compared with the data from 2000 to 2015, except in the NC and MYR (Fig. 5a). This is due to the significantly deeper groundwater in these two regions compared to other regions, such that they do not yet reflect the short-term nitrogen control measures. In other words, it would take longer time for nitrogen management practices to become effective in deeper groundwater[18]. This reflects the complexity of transport and the persistence of legacy nitrogen, reinforcing the notion that recovery is gradual and varies depending on soil depth, land use, and hydrogeological characteristics[52,67,68]. There has been a significant reduction in agricultural nitrogen input in these two regions (Fig. 5b), indicating that the current agricultural treatment measures will have positive implications for the mitigation of groundwater nitrogen pollution in the future.

(29). Fig 5: this is a very confusing figure. Why are the symbols connected by lines? This is not a time series progression but rather, these are economic regions that may or may not be connected. The important differences are the two time periods. We don't know if the variability among time periods is small enough to indicate actual statistical differences from one time period to the next because there are no error bars and no associated statistical tests especially for 5a.

Re: Thank you for your valuable feedback. We appreciate your suggestions and have revised Fig. 5 accordingly. The lines connecting symbols were removed to avoid misleading impressions of the temporal progression between economic regions. We have also added error bars to better highlight the differences between the two periods (See Lines 360-367 and Lines 379-388).

Lines 360-367:

Although the data used in this study are based on single sampling events, the data points across different economic zones are widely distributed between 2000 and 2015 and 2016–2020 (see the numbers of samples in different economic zones from 2000 to 2020 in Fig. 1a and Table S5). To better capture temporal variations, we also calculated the overall means and standard deviations (SD) for the two periods: 2000–2015 and 2016–2020 (Fig. 5). Notably, overall groundwater nitrogen pollution significantly declined during 2016–2020 compared with the data from 2000 to 2015, except in the NC and MYR (Fig. 5a).

Lines 379-388:

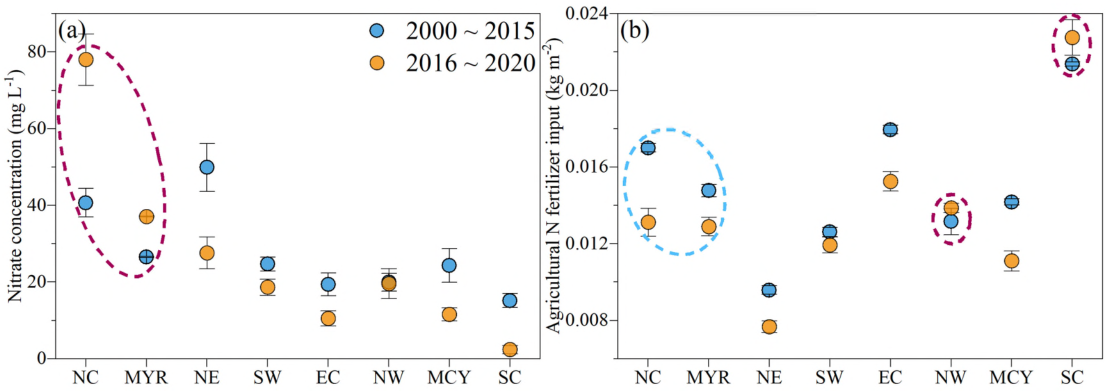

Fig. 5 Regional-level changes of groundwater nitrate concentration and agriculture N fertilizer input in 2000 ~ 2015 and 2016 ~ 2020. (a) Comparison of groundwater nitrate concentration in eight economic regions in 2000 ~ 2015 and 2016 ~ 2020. (b) Comparison of per-unit agriculture N fertilizer input in eight economic regions in 2000 ~ 2015 and 2016 ~ 2020. This broad spatial coverage is crucial for capturing the major regional trends in nitrogen pollution, adequately representing the two distinct periods. Blue circle and yellow triangles indicate the 2000 ~ 2015 and 2016 ~ 2000, respectively. Blue shading (and red ellipse) represents the value of 2016 ~ 2020 is higher than that of 2000 ~ 2015, and vice versa in green shading (and blue ellipse).

(30). **PL360**: change intake to uptake

Re: Thank you very much for your suggestion. We have revised this (See Lines 399-400).

Lines 399-400:

In theory, shallow groundwater with short retention time[69] and vegetation uptake[51] offer more efficient removal of nitrogen pollution compared to deep groundwater.

(31). **PL370**: in addition to low DO, there appears to more DOC at deeper depths which could better fuel denitrification

Re: Thank you for your insightful observation. We have revised the manuscript to incorporate your suggestion, noting that higher levels of dissolved organic carbon (DOC) at deeper depths could further enhance denitrification (See Lines 432-435).

Lines 432-435:

Specifically, more anoxic conditions and lower DOC (Fig. 6c-d and Fig. S2) in groundwater with increasing depth can well explain the increase of $\delta^{15}N\text{-}NO_3^-$ by denitrification in the previous period in the early stage (Fig. 3d), which is also consistent with our previous hypothesis.

(32). **PL443**: when referencing the nitrogen cascade, please cite Galloway 2003. Would be useful for the reader to know what the N cascade is so that this statement has context.

Re: Thank you very much for your suggestion. We have revised this (See Lines 481-482).

Lines 481-482:

In addition, our analyses reveal the frequently overlooked impact of aquifer depth on the strength of the nitrogen cascade[79].

(33). **PL456**: what are the published papers? Would like to see the references and know how these wells were sampled, frequency of sampling, variability, etc.

Re: Thank you for your valuable feedback. We have revised the manuscript based on your suggestions. All data, including their sources, sampling methods, frequencies, and variability, are provided in the supplementary data.

(34). Lit cited

Noticing inconsistent lit cited formats, e.g. 8: Nature Communications; 12 Communications Earth and Environment

Re: Thank you for your comment. We have revised the citation format to ensure consistency and aligned it with the journal's guidelines.

Reply to Reviewer #1's major comments:

Reviewer #1 (Remarks to the Author):

(1). After going through the response letter, article and SI, I still have doubts about how data representing the time period 2000-2020 are used in combination with the spatial datasets that probably represent one single year. For example, population has grown by about 16% between 2000 and 2020. Probably there have been also changes in climate, soil N, soil pH, and other dynamic soil properties. I suggest that the authors show that the impact of such changes is small and can be neglected in the analysis presented, supported by literature, for all those factors that are variable.

Reply: Thank you for your valuable suggestion regarding the potential mismatch between temporal datasets and spatial variables and its implications for the analysis. We provide the following clarifications on this issue. (i) Population: Although the population growth rate between 2000 and 2020 is about 16%, in this study, we used the average of the population in each region during 2000 ~ 2020, and the influence of human activities on groundwater nitrogen dynamics is mainly through indirect channels (such as increased agricultural intensity or land use change), which has been analyzed in this study. (ii) Climate: Averages of the multi-year climate datasets (such as temperature and precipitation from 1982 ~ 2015) used in this study, thus essentially reflecting the influence of the sampling sites on groundwater nitrogen dynamics. (iii) Soil properties (nitrogen, pH, etc.): While some soil properties (e.g., nitrogen and pH) may change spatially and temporally as a result of agricultural activities and environmental changes, their large-scale patterns are generally stable over the time frame considered. Previous studies[1,2] have demonstrated that inter-annual variability in soil properties is typically smaller than regional-scale spatial variability. We hope this clarification and additional analysis address the reviewer's concerns. (See Lines 519-524, Lines 526-529)

Lines 519-524:

The land use types were mainly divided into natural, cropland, and urban areas (Fig. S11), and the average population density from 2000 to 2020 was divided into four categories according to the quartile method of sampling site distribution: < 56-person km^{-2} (low), 56 ~ 316-person km^{-2} (medium), 316 ~ 956-person km^{-2} (high), > 956-person km^{-2} (very high) (Table S6 and Fig. S12)

Lines 526-529:

The mean annual precipitation (Fig. S13) and mean annual temperature (Fig. S14) for 1982 ~ 2015 were obtained from the China Meteorological Administration (CMA) (http://data.cma.cn/) with a spatial resolution of 0.25° × 0.25°.

(2). I had a question about the lithology (which in the SI is listed under topography), and the authors responded as follows: "In this study, the random forest model data did not include lithology as a factor". Does that mean that lithology was not considered (so why is it in the list), or did it not come out as a significant or important factor? In that case, it may be good to state that only significant/important factors are considered and to include the list of significant and non-significant factors.

Reply: Thank you very much for your question regarding lithology. In this study, lithology was one of the 66 spatially continuous environmental variables considered. However, it ranked 60th in importance and did not show a significant influence on nitrate dynamics. In the manuscript, we have now included a detailed ranking of all variables by their importance in the analysis and clarified in the manuscript that only significant and impactful factors were further considered. This addition ensures transparency in the selection process and highlights the relative contributions of each variable. (See ***Supplementary information*** **(SI)** Lines 201-204)

SI Lines 201-204:

Table S2. Spatially continuous environmental variables considered in the analysis and prediction of nitrate concentrations in groundwater. The relative importance of 66 variables for groundwater nitrate concentrations was determined by regression forecasting using random forests. The columns marked * (P < 0.05) and ** (P < 0.01) represent drivers have significant impacts on nitrate concentrations; at the equator, 30" is approximately equal to 1 km; "-" represents no unit.

Type	Short name	Full name	Importance	Unit	Resolution	Reference
Soil	TSN	Total Soil Nitrogen (0 ~ 200 cm)	27.9**	g kg^{-1}	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	WS	Wind Speed	23.2**	m s^{-1}	0.05° × 0.05°	https://data.casearth.cn/sdo/detail/6123651428a58f70c2a51e49
Climate	BIO15	Precipitation Seasonality (Coefficient of Variation)	22.9**	mm	30' × 30'	https://worldclim.org/data/worldclim21.html
Soil	SAND	Sand Content (0 ~ 200 cm)	22.0**	%	250 m × 250 m	https://zenodo.org/records/1464846#.YoXUVOhBw2w
Climate	BIO3	Isothermality	21.5**	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	SR	Solar Radiation	21.3**	kJ m^{-2} day^{-1}	250 m × 250 m	https://zenodo.org/records/1447210
Vegetation	LAI	Leaf Area Index	20.2*	-	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1566

Soil	VWC	Volumetric Water Content (0 ~ 200 cm)	20.1**	%	1 km × 1 km	https://developers.google.com/earth-engine/datasets/catalog/MODIS_061_MOD17A3HGF
Soil	SOC	Soil Content Carbon (0 ~ 200 cm)	20.0*	g kg^{-1}	250 m × 250 m	https://zenodo.org/records/1447210
Soil	CEC	Cation Exchange Capacity (0 ~ 200 cm)	19.1**	cmol kg^{-1}	30' × 30'	https://worldclim.org/data/bioclim.html
Topography	Elevation	Elevation	18.6**	m	30' × 30'	https://worldclim.org/data/bioclim.html
Soil	SILT	Silt Content (0 ~ 200 cm)	18.0*	%	250 m × 250 m	https://zenodo.org/records/1447210
Climate	BIO4	Temperature Seasonality	17.5**	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Vegetation	GPP	Gross Primary Productivity	16.8	kg C m^{-2} $year^{-1}$	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Climate	BIO12	Annual Precipitation	16.7**	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Climate	BIO13	Precipitation of Wettest Month	16.4**	mm	30' × 30'	https://worldclim.org/data/worldclim21.html
Soil	OCS	Organic Carbon Stocks (0 ~ 200 cm)	16.3	kg m^{-2}	250 m × 250 m	https://zenodo.org/records/1447210
Climate	VAPOR	Water vapor pressure	16.3**	kPa	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Climate	BIO17	Precipitation of Driest Quarter	15.9**	mm	30' × 30'	https://worldclim.org/data/bioclim.html

Climate	BIO19	Precipitation of Coldest Quarter	15.9**	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Topography	GRR	Groundwater Recharge Rate	15.8	m $year^{-1}$	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Climate	BIO18	Precipitation of Warmest Quarter	15.6*	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Soil	CLAY	Clay Content	15.5	%	30' × 30'	https://worldclim.org/data/bioclim.html
Topography	VBF	Valley Bottom Flatness	15.4	-	0.05° × 0.05°	https://doi.org/10.1038/ngeo1617
Climate	BIO16	Precipitation of Wettest Quarter	14.9**	mm	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	AI	Aridity Index	14.7**	-	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Climate	BIO8	Mean Temperature of Wettest Quarter	14.6	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO10	Mean Temperature of Warmest Quarter	14.4*	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Soil	PH	Soil pH (0 ~ 200 cm)	14.3*	-	250 m × 250 m	https://zenodo.org/records/1447210
Climate	BIO5	Max Temperature of Warmest Month	14.2	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	ET	Potential Evapotranspiration	14.0	mm	30' × 30'	https://worldclim.org/data/worldclim21.html
Topography	TWI	Topographic Wetness Index	13.9	-	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01621-x

Climate	ETsd	Potential Evapotranspiration sd	13.8*	mm	1 km × 1 km	https://landscan.ornl.gov/
Climate	BIO7	Temperature Annual Range	13.4*	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO2	Mean Diurnal Range	13.3	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO9	Mean Temperature of Driest Quarter	12.7	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Soil	OCD	Organic Carbon Density (0 ~ 200 cm)	12.6	hg dm^{-3}	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Topography	DVM	DVM2	12.5	-	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	MAT	Temperature Mean	12.4*	°C	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	WDR	Groundwater depletion rate	12.4*	mm yr^{-1}	0.08° × 0.08°	https://www.resdc.cn/data.aspx?DATAID=336
Climate	TMAX	Temperature Max	12.0	°C	250 m × 250 m	https://zenodo.org/records/1447210
Soil	BDOD	Bulk Density (0 ~ 200 cm)	11.8	kg dm^{-3}	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Soil	CFVO	Volumetric Fraction of Coarse Fragments (0 ~ 200 cm)	11.8	volume %	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	MAP	Precipitation	11.5**	mm	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated

Climate	BIO11	Mean Temperature of Coldest Quarter	11.1	°C	30' × 30'	https://worldclim.org/data/worldclim21.html
Topography	UVB	Upland Valley-bottom and Lowland Sedimentary Deposit Thickness	11.0	m	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304
Climate	BIO1	Annual Mean Temperature	10.9	°C	1 km × 1 km	http://dx.doi.org/10.1038/s41597-022-01493-1
Climate	BIO6	Min Temperature of Coldest Month	10.5	°C	30' × 30'	https://worldclim.org/data/bioclim.html
Vegetation	LUT	Land Use Types	9.7	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	Curvature	Curvature	9.3	-	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	TMIN	Temperature Min	9.0	°C	250 m × 250 m	https://zenodo.org/records/1447210
Topography	DC	Downlslope Curvature	8.5	-	30' × 30'	https://worldclim.org/data/bioclim.html
Climate	BIO14	Precipitation of Driest Month	8.2	mm	30' × 30'	https://worldclim.org/data/worldclim21.html
Topography	HSVB	Hill-slope Valley-bottom	8.1	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	MRN	MRN	7.7	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	UPCUR	Upslope Curvature	7.7	-	1 km × 1 km	https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1304

Topography	SSDT	Average Soil and Sedimentary-deposit Thickness	7.5	m	250 m × 250 m	https://zenodo.org/records/1447210
Topography	Landform	Landform	7.2	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	TPI	Topographic Position Index	6.4	-	250 m × 250 m	https://zenodo.org/records/1447210
Topography	Lithology	Lithology	6.4	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	Slope	Slope	6.3	°	250 m × 250 m	https://zenodo.org/records/1447210
Topography	POS	POS	5.7	-	250 m × 250 m	https://zenodo.org/records/1464846#.YoXUVOhBw2w
Soil	HYSOGs	Global Hydrologic Soil Groups (0 ~ 200 cm)	5.2	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Topography	LC	Land Cover Mask	4.9	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated
Human activities	PD	Population Density	3.7	People km^{-2}	250 m × 250 m	https://zenodo.org/records/1447210
Topography	NEG	NEG	3.6	-	1 km × 1 km	https://files.isric.org/soilgrids/latest/data_aggregated

(3). A third issue which confuses me is “In addition, the RF model based on Gini index was employed to calculate the importance score of 11 variables (including GW depth, TDS, EC, MAT, longitude, ecoregion, MAP, T-water, latitude, and pH) on nitrate dynamics.” First of all, I count 10 variables in this sentence.

Reply: Thank you for pointing out the inconsistency in the number of variables listed. We have carefully reviewed and revised this section to accurately reflect the variables used in the RF model. (See Lines 546-548)

Lines 546-548:

In addition, the RF model based on Gini index was employed to calculate the importance score of 10 variables (GW depth, TDS, EC, MAT, longitude, ecoregion, MAP, T-water, latitude, and pH) for nitrate dynamics.

(4). In the methods I read the following: “Here we used decision-tree heatmaps to predict the threshold values of different nitrate concentrations using the "treeheatr" package based on the interactions among aquifer depth, population density, land use, and ecoregion characteristics. In addition, the structural equation model was used to explore the occurrence regularity of nitrate dynamics under different geographical and climate factors. Geographical (including ecoregion, latitude, and longitude) and climate factors (including MAP and MAT), groundwater aquifer depth, TDS, pH, EC, and T-water were set as the variables.” I see that the second list is from observations at the monitoring sites (e.g., observations), while the first list is data from the spatially explicit maps (e.g., auxiliary data, instead of "external factors" in line 272). I suggest that the authors re-organize the text and methods to make this distinction clear and to argue the purpose of each analysis.

Reply: Thank you for your valuable suggestion. We have revised the manuscript and methods section to clearly distinguish between the two datasets: auxiliary data (including geographical (including ecoregion, latitude, and longitude), climate factors (including MAP and MAT), and hydrochemical characteristics (including TDS, pH, EC, and T-water)), aquifer depth. The purpose of each analysis has also been clarified, highlighting how the observational data were used for structural equation modeling and how the spatially explicit data supported decision-tree heatmap predictions. These changes ensure that the distinction and rationale for each dataset are more explicit. (See Lines 607-615)

Lines 607-615:

Structural equation modeling is hypothesis driven, focusing on causal relationships and the direct, indirect, and total effects between variables through path coefficients. It is well suited for validating theoretical frameworks and understanding the mechanisms behind variable interactions. In this study, auxiliary data (including geographical (including ecoregion, latitude, and longitude), climate factors (including MAP and MAT), hydrochemical characteristics (including TDS, pH, EC, and T-water)), and aquifer depth were set as the variables. Correlations and contributions between variables were analyzed using Amos software[86].

(5). I do not quite understand what "structural equation mode" is, and occurrence regularity". Is the structural equation model different from the RF model? So please check this and make consistent.

Reply: Thank you very much for your suggestion. Structural Equation Modeling (SEM) and Random Forest (RF) differ significantly in assessing variable importance due to their theoretical foundations, methodologies, and applications. Structural equation modeling is hypothesis-driven, focusing on causal relationships and the direct, indirect, and total effects between variables through path coefficients. It is well-suited for validating theoretical frameworks and understanding the mechanisms behind variable interactions. In contrast, random forest is data-driven, relying on measures like Gini impurity or prediction error to evaluate variable importance based on their contribution to model performance. While random forest excels at handling non-linear relationships, complex interactions, and high-dimensional data, it does not infer causal relationships. In this study, random forest model based on Gini index was employed to calculate the importance score of 10 variables (including GW depth, TDS, EC, MAT, longitude, ecoregion, MAP, T-water, latitude, and pH) on nitrate dynamics. Structural equation modeling requires strict assumptions, such as linearity and normality, and is ideal for hypothesis testing, whereas random forest is more flexible and commonly used for exploratory analysis and prediction. Combining both methods can provide complementary insights, with structural equation modeling clarifying causal pathways and random forest identifying key predictors. (See Lines 534-538 and Lines 607-611)

Lines 534-538:

As an integrated machine learning method and bagging algorithm, the random forest can effectively quantify the relative importance of each factor to reveal potential influence mechanisms[68]. RF model has been frequently applied in environmental science to map nitrate distributions and identify key influencing factors and control mechanisms.

Lines 607-611:

Structural equation modeling is hypothesis driven, focusing on causal relationships and the direct, indirect, and total effects between variables through path coefficients. It is well suited for validating theoretical frameworks and understanding the mechanisms behind variable interactions.

(6). Finally, the text needs serious editing by a native English speaker, also to remove inconsistent use of terms and other inconsistencies. My advice is often: try to explain this to a layman (e.g., a family member).

Reply: Thank you very much for your suggestion. We have thoroughly revised the manuscript to improve readability and eliminate inconsistencies. Additionally, the revised manuscript has been carefully edited by coauthors, e.g., Prof Li Li working in The Pennsylvania State University and Dr Wei Wen Wong working in Monash University to enhance its linguistic quality.

References

1 Ren, Y. *et al.* China's wetland soil organic carbon pool: New estimation on pool size, change, and trajectory. *Global Change Biol.* **29**, 6139-6156, (2023).

2 Zhang, Z. *et al.* Historical and future variation of soil organic carbon in China. *Geoderma* **436**, 116557, (2023).