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Electrical conductivity as a reliable indicator for assessing land use effects on stream N_2O concentration

Sibo Zhang [a], Xinghui Xia [b,*], Yuan Xin [b], Xiaokang Li [c], Junfeng Wang [b], Leilei Yu [b], Cangbai Li [a], William H. McDowell [d], Qian Tan [a], Zhifeng Yang [a,*]

[a] Guangdong Provincial Key Laboratory of Water Quality Improvement and Ecological Restoration for Watersheds, Institute of Environmental and Ecological Engineering, Guangdong University of Technology, Guangzhou, 510006, China
[b] Key Laboratory of Water and Sediment Sciences of Ministry of Education/State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, China
[c] School of Environmental and Material Engineering, Yantai University, Shandong 264005, China
[d] Department of Natural Resources and the Environment, University of New Hampshire, Durham, New Hampshire, USA

A R T I C L E I N F O

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A B S T R A C T

While it is widely acknowledged that different categories of terrestrial land use significantly affect N_2O emissions from streams and rivers, a suitable indicator to comprehensively reflect such influences is still lacking. This study examined the effectiveness of stream environmental and microbial factors in reflecting the influence of land use types on stream N_2O concentrations, taking into account both endogenous N_2O production and exogenous N_2O inputs. Our results showed that human-disturbed (urban and agricultural) streams had nearly four times higher excess N_2O concentrations (ΔN_2O) than forest streams (5.01 versus 1.32 nmol/L N_2O). By combining our observations with previous studies, we identify electrical conductivity as a significant and even the strongest predictor of (excess) N_2O concentration and flux in streams across different land uses, surpassing the predictive power of nitrogen content. Elevated ΔN_2O was observed at higher conductivities ($r = 0.69$, $p < 0.01$), which coincided with higher carbon and nutrient levels across different types of land use. Also, conductivity was positively correlated with the abundance of N_2O-producing microbes ($p < 0.05$), including both nitrifying and denitrifying microbes. Denitrifiers adapted to human disturbance and the genetic potential for net N_2O production, as evidenced by the positive correlation between conductivity and *nir*:*nosZ* ratio, were enhanced under high-conductivity conditions ($p < 0.05$). Furthermore, electrical conductivity had great potential to qualitatively indicate the magnitude of exogenous N_2O input across different land uses. Overall, our results highlight the value of electrical conductivity as a reliable indicator for assessing the effect of land use types on stream N_2O concentrations. This opens opportunities for the development of simple field-based assessments of riverine N_2O emissions across regional landscapes.

1. Introduction

Nitrous oxide (N_2O) is a prominent stratospheric ozone-depleting substance and a potent greenhouse gas, with a global warming potential approximately 300 times greater than that of carbon dioxide on a 100-y ear timescale (Ravishankara et al. 2009). River systems are major sources of N_2O emissions, converting at least 680 Gg of anthropogenic N inputs to N_2O-N per year, equivalent to 10 % of the global anthropogenic N_2O emissions (Beaulieu et al. 2011). Low-order rivers (hereafter referred to as streams) are estimated to contribute up to 85 % of global riverine N_2O emissions (Yao et al. 2020). Extensive research has demonstrated that terrestrial land use types are highly relevant to, or even exert major controls on, the magnitude of stream N_2O emissions, with human-disturbed streams emitting N_2O at higher rates than pristine streams (Herreid et al. 2021; Hu et al. 2016).

Human-disturbed streams, in comparison to pristine streams, receive higher inputs of carbon and nutrients. For example, agricultural and urban streams have been found to have higher concentrations of nitrate and ammonium than forested streams (Hu et al. 2016). In addition, land use modification and related anthropogenic activities are major drivers

* Corresponding authors.
E-mail addresses: xiaxh@bnu.edu.cn (X. Xia), zfyang@gdut.edu.cn (Z. Yang).

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of microbial change worldwide (Petsch et al. 2021). Although limited efforts have been made in this area, researchers have found an increase in the abundance of genes related to nitrification and denitrification in human-disturbed streams, which are responsible for N_2O production in river systems (Beaulieu et al. 2011; Chen et al. 2023). Furthermore, the exogenous input of N_2O to streams is expected to increase in human-disturbed areas compared to pristine areas (Que et al. 2023). Some studies have even identified wastewater treatment plant effluent as a direct contributor to N_2O emissions in certain urban streams (Que et al. 2023). Together, these factors contribute to the higher N_2O emission rates from human-disturbed streams compared to pristine streams.

As land use practices continue to evolve and diversify, it becomes crucial to identify appropriate variables that will comprehensively reflect the effect of land use on riverine N_2O emissions for accurate prediction of both current and future N_2O emissions from river systems. Stream electrical conductivity has been observed to increase in conjunction with the expansion of urban land cover (Que et al. 2023) and agricultural intensity (Atwell and Bouldin 2022) within catchments. Consequently, enhanced carbon and nitrogen inputs to human-disturbed streams are frequently accompanied by introduction of water possessing higher conductivities. Previous studies have found that elevated levels of sulfide and ferrous ions could facilitate the prevalence of chemoautotrophic denitrification and the enhancement of N_2O production (Hu et al. 2020). The enrichment of sulfide and ferrous ions has been consistently observed in urban and agricultural streams with higher electrical conductivities (Shupe 2017; Zhang et al. 2023) compared to

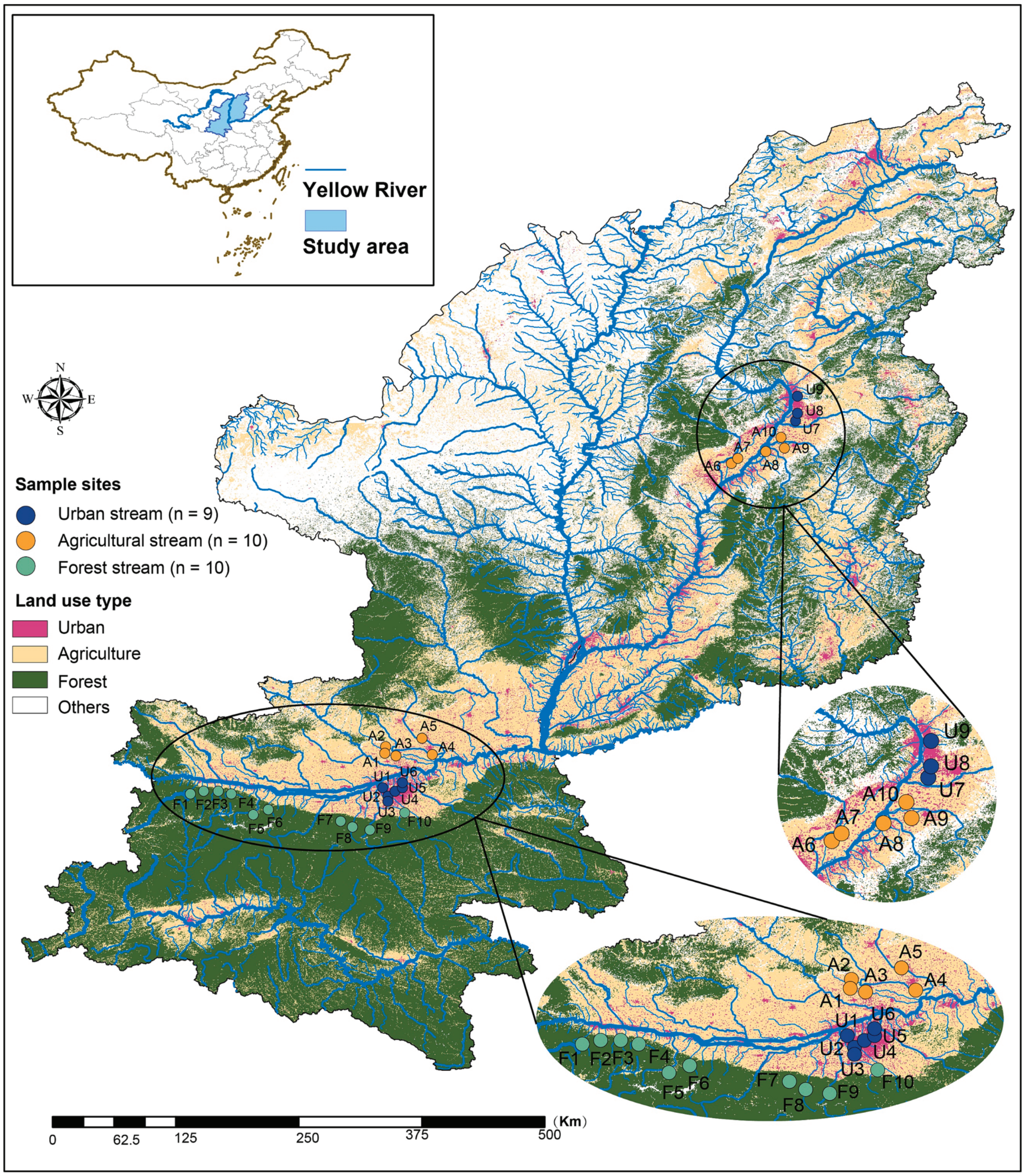

Fig. 1. Map of the 29 surveyed streams located in the Yellow River watershed. Detailed information is available in Table S1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

forest streams within the same watershed. Therefore, it is anticipated that increased electrical conductivities would align with elevated N_2O production from chemoautotrophic denitrification in streams. Beyond the stream channel, different sources of stream water typically exhibit significant variation in electrical conductivity (Calvi et al. 2018; Carey et al. 2014), with baseflow water displaying higher conductivities than runoff, and electrical conductivity becoming diluted as runoff volume increases. Under such circumstances, elevated electrical conductivities potentially represent prolonged contact time of external water with soils (Cheng et al. 2020; Winnick 2021), suggesting a greater potential for exogenous N_2O production and influx into streams. Collectively, it is believed that electrical conductivity could serve as a reliable indicator for evaluating the influence of land use on stream N_2O concentration.

This study was conducted to assess the potential of using electrical conductivity as an indicator of N_2O concentration in streams across different land use types. Initially, we performed a thorough investigation of the effects of different terrestrial land uses, including forest, urban, and agriculture, on key environmental factors, microbial composition and functionality, and N_2O characteristics. We then carefully examined the importance of environmental factors in discriminating differences in N_2O levels between forested and human-disturbed (urban and agricultural) streams, with a particular focus on electrical conductivity. This analysis draws upon our own data and an extensive synthesis of prior research. Subsequently, we analyzed the feasibility and rationality of electrical conductivity in indicating the effect of land use on stream N_2O concentrations by considering both endogenous N_2O production and exogenous N_2O inputs.

2. Methods

2.1. Site description, sample collection, and physicochemical characteristic analysis

With the aid of Google Earth, a total of 29 low-order streams (33.95–37.99 °N; 107.03–112.58 °E) within the Yellow River watershed were selected and sampled in August 2021 (Fig. 1 and Table S1). The average water depth of our sampled streams was ~ 40 cm. The 29 streams spanned different terrestrial land uses (Table S1). Based on the dominant land cover, these streams were divided into agricultural (n = 10), urban (n = 9), and forest (n = 10) stream categories (Fig. 1), each with a dominant land cover proportion greater than 58 % of the total catchment area.

During the sampling period, stream water temperature, dissolved oxygen (DO), electrical conductivity (hereafter referred to as conductivity), oxidation–reduction potential (ORP), and pH were monitored *in situ* using a HACH (USA) HQ2100 portable meter. Surface (~20 cm depth) water samples were collected using acid-washed polyethylene bottles for analysis of chemical properties. Stream surface (0–5 cm) sediment samples were collected and then divided into two parts. One subsample was stored at − 20 °C for physicochemical analysis, and the other was flash-frozen and stored in liquid nitrogen for biological analysis. Unlike water samples, sediment samples were not accessible in four urban streams.

Physicochemical analysis of sediment and water samples was completed within 14 days of being returned to the laboratory. For water samples, concentrations of dissolved organic carbon (DOC), total phosphorus (TP), NH_4^+, and NO_3^- were determined. For sediment samples, we measured the pH, median sediment particle size (D50), carbon and nitrogen levels (sediment organic matter (SOC) and total nitrogen (TN), NH_4^+, and NO_3^-), and the ferrous ion (Fe^{2+}) and sulfide (S^{2-}) contents. The analytical methods are described in Supplementary Text 1.

2.2. Determination of N_2O concentration and flux and incubation experiments with varying NO_3^- concentrations

To determine the dissolved N_2O concentration, triplicate water samples were collected at each site using 120-ml glass serum vials, with 2 ml of a 50 % (*w/v*) $ZnCl_2$ solution added to inactivate microbial activity. Within 1 h after sample collection, 30 ml of high-purity nitrogen (>99.999 %) was introduced to each glass vial, replacing an equivalent volume of water. Vials were then vigorously shaken for 20 min to equilibrate gases between the water and headspace. The headspace gas was extracted with a gas-tight syringe and injected into a pre-evacuated 20-ml aluminum foil airbag (Delin, China). The gas samples were determined by a gas chromatograph with an electron capture detector (Agilent 7890B, GC-ECD), and the dissolved concentration of N_2O in water samples was calculated according to the procedure described in our previous research (Wang et al. 2022). Excess N_2O concentration (ΔN_2O = N_2O(observed) - N_2O(equilibrium)) in water samples was obtained as the difference between the observed N_2O concentration and N_2O equilibrium concentration calculated based on local temperature, salinity, and air pressure (Wang et al. 2022).

Sediment cores were collected from the sampling sites using a gravity sediment corer with a tube length of 60 cm and an inner diameter of 9 cm. Sediment porewater was extracted *in situ* from 5, 10, 15, 20, 25 cm depth below the sediment–water interface. The porewater was extracted through holes drilled in the side wall of the core using Rhizon tubes (pore size of 0.15 μm, Rhizosphere Research Products B.V., Netherlands) connected to pre-evacuated vials (40 ml volume) to ensure minimal cross-contamination between sediment layers (Sun et al. 2022). In the field, a total of 20 ml of the extracted porewater was removed using a syringe with a three-way valve and replaced with a headspace filled with high-purity nitrogen. To achieve equilibrium between the porewater and headspace gases, the samples were shaken vigorously for 5 min before the headspace N_2O concentrations measured using GC-ECD. Porewater N_2O concentrations were calculated using the same method as for overlying water samples. The N_2O flux at the water–air interface was measured using a floating chamber method (Wang et al. 2022), and detailed procedures are provided in Supplementary Text 2.

Incubation experiments were performed to investigate the effect of NO_3^- concentration on endogenous N_2O production. This incubation was initiated with a series of N_2O additions but contained only sediment-carried NO_3^-. Approximately 2.5 g of fresh sediment was added into 12-ml Labco Exetainer vials, followed by the addition of synthetic river water (pH: ~7.4) (Zhang et al. 2021), with a final headspace volume of 6 ml. To create anoxic conditions and eliminate background N_2O, the vials were flushed with high-purity argon (>99.999 %) for at least 10 min. Varying amounts of N_2O were then injected into the vials. To achieve this goal, stock N_2O from a gas cylinder (mole fraction: ~ 4,800 ppm) was serially diluted with argon (0, 1/200, 1/100, 1/40, and 1/10) by transferring specific volumes of stock N_2O into pre-evacuated aluminum foil airbags (Delin, China). Subsequently, 100 μl of the diluted N_2O in the airbag was injected into the vials, with the final dissolved N_2O concentration varying between 5 and 270 nmol/L, and each dilution gradient was constructed in triplicate. These vials were then incubated in the dark on shakers at 150 rpm and exposed to corresponding local water temperatures. Incubations lasted for up to 12 h and were sacrificially sampled in triplicate at 0 h, 1 h, 3 h, 6 h, and 12 h, and the headspace N_2O was measured on an Agilent 7890B (GC-ECD). In a separate set of incubation vials, specific amounts of NO_3^- were added in addition to N_2O to achieve a final concentration in the vial of 3 mg-N L^{-1}, slightly above the average *in situ* dissolved inorganic nitrogen (DIN) content of 2.5 mg/L. Their incubation, sampling, and determination were the same as for the incubations without NO_3^- addition. Net N_2O transformation rates were calculated based on the linear variation of N_2O within the sampling period.

2.3. DNA extraction, qPCR quantification, and high-throughput sequencing

Triplicate genomic DNA from fresh sediment samples at each site was extracted using the FastDNA SPIN Kit for Soil (MP Biomedicals, CA, USA) following the manufacturer's instructions. The DNA quality and concentration were roughly determined using a NanoDrop 2000 UV–visible spectrophotometer (Thermo Scientific).

To estimate the genetic potential of N_2O production and reduction ($N_2O \rightarrow N_2$) in sediment samples, qPCR assays targeting the corresponding functional genes were conducted in triplicate on a C1000™ thermal cycler (Bio-Rad, USA). Specifically, bacterial and archaeal *amoA* (ammonia monooxygenase subunit A) genes were used to assess the nitrifying microbial N_2O production potential (Bahram et al. 2022); *nirS* and *nirK* (two types of nitrite reductase) genes were employed to estimate the denitrifying bacterial N_2O production potential (Bahram et al. 2022); clade I *nosZ* (N_2O reductase, hereafter called *nosZ*I) and clade II *nosZ*II (hereafter called *nosZ*II) genes were targeted to evaluate the N_2O reduction potential (Bahram et al. 2022). Ten-fold serial dilutions of plasmid DNAs, generated by amplification of the targeted genes from extracted DNA, were used to construct quantification curves. Detailed information on the primer pair, qPCR reaction mixture, and thermal profile is provided in Table S2. The R^2 of all standard curves was greater than 0.98, and the PCR efficiencies were 65–97 % (Table S2). For the denitrification community analysis, both *nirS* and *nirK* gene libraries were constructed using the same primer pair as in the qPCR assays (Table S2). Subsequently, the *nirS* and *nirK* gene amplicons were sequenced on an Illumina MiSeq PE300 platform at Majorbio Genomics Institute (Shanghai, China).

2.4. Sequence processing and microbial diversity analysis

Raw sequences were assigned to their corresponding sampling sites based on barcode information. The UPARSE pipeline (Edgar 2013) implemented in USEARCH v7.0 was used to construct operational taxonomic unit (OTU) tables with an 88 % nucleotide similarity cutoff (Zhang et al. 2021). Prior to community diversity calculation, to avoid the bias introduced by varying sequencing depth, the *nirS* and *nirK* gene libraries were resampled while retaining a maximum number of reads. After quality filtering and resampling analysis, a total of 22,513 *nirS* and 18,845 *nirK* gene sequences were retained for each sample.

Differentiation of denitrifying bacterial communities among the forest, agricultural, and urban streams was presented using Bray-Curtis distance-based principal coordinates analysis (PCoA) ordination plots in the 'vegan' package v2.5.7 (Oksanen et al. 2013) of R software (v4.1.0) (R Core Team 2013) and verified by analysis of similarities (ANOSIM). Mantel correlations between denitrifying bacterial communities and physicochemical factors were calculated and displayed using the 'vegan' and 'linkET' packages (https://github.com/Hy4m/linkET), respectively. The contribution of each physicochemical and spatial factor to denitrifying bacterial community variation was calculated in the 'rdacca.hp' package (Lai et al. 2022). Patterns of variation in *nirS* and *nirK* community compositions along the conductivity gradient were explored using TITAN (Threshold Indicator Taxa Analysis) (King and Baker 2014). The preference of *nirS*- and *nirK*-type denitrifier OTUs for low- and high-conductivity habitats was identified by Songbird analysis (Morton et al. 2019), following the pipeline described at https://github.com/biocore/songbird. The differential rank of each OTU was determined to represent the ordering of OTUs in terms of how closely they are associated with a particular variation. Our models exhibited good performance, with pseudo-Q^2 values of > 0.11 for the *nirS*-type denitrifier community and of > 0.10 for the *nirK*-type denitrifier community.

2.5. Statistical analysis

In this study, principal component analysis was conducted to identify differences in physicochemical properties between different stream categories. Redundancy analysis (RDA) in the 'vegan' package was employed to investigate the factors constraining the spatial variation in N_2O-related microbial abundance. A non-parametric Kruskal-Wallis test was used to evaluate the differences in N_2O concentration and flux between different stream categories. Spearman's correlation analysis was used to compare the strength of the correlation between physicochemical factors, microbial abundance, and N_2O.

To assess the respective power of physicochemical and microbial factors in predicting ΔN_2O, stepwise multiple linear regression analysis was performed using the 'dredge' command in the 'MuMIn' package (Barton and Barton 2015). To test the applicability and rationality of linear relationship fitting, we conducted scatter plots between ΔN_2O and each predictor and performed the necessary log-transformations to guarantee the superiority of linear fitting analysis. Partial least squares (PLS) path modeling was constructed using SmartPLS 3 software (Boenningstedt, Germany) to explore the hierarchical control of physicochemical and microbial factors on stream ΔN_2O. The path model used 1,000 bootstraps to validate the estimates of path coefficients and the coefficients of determination (R^2). The PLS path model analysis achieves high levels of statistical power with small sample sizes (Hair et al., 2021), and the PLS results were verified by partial correlation analysis. The individual power of denitrification community to explain the variance in ΔN_2O was examined by variance partitioning analysis using the 'varpart' function in the 'vegan' package (Oksanen et al. 2013).

3. Results and discussion

3.1. Concurrent changes in conductivity and other physicochemical properties

The physicochemical properties of both water and sediment samples displayed substantial disparities between forest and human-disturbed streams (i.e., agricultural and urban streams) (Fig. 2a-b). In contrast, there were no apparent differences between agricultural and urban streams (Fig. 2b). Consistent with previous research (Liang et al. 2023; Que et al. 2023), a concurrent increase of carbon, nutrients, and electrical conductivity was observed from forest streams to human-disturbed streams. Specifically, for water samples, forest streams had significantly lower levels of DOC (4.12 versus 6.87 mg-C L^{-1}, on average), TP (0.03 versus 0.26 mg-P L^{-1}), and conductivity (350 versus 1,443 μS cm^{-1}) (Table S3) compared to human-disturbed streams (Wilcoxon test, $p < 0.05$). Although there were no significant differences in NH_4^+-N and NO_3^--N concentrations between these categories of streams ($p > 0.1$), their maximum values were observed in agricultural or urban streams (Table S3). The PCoA results showed that conductivity was a crucial factor associated with the differentiation of water physicochemical properties between human-disturbed and forest streams.

Sediments from human-disturbed streams had significantly higher contents of total nitrogen (1.14 g-N kg^{-1} versus 0.20 g-N kg^{-1}) and organic carbon (9.58 g-C kg^{-1} versus 2.09 mg-C kg^{-1}) compared to forest streams (Fig. 2b and Table S4). Besides carbon and nitrogen, sulfide (S^{2-}, 381.1 versus 4.7 mg kg^{-1}) and ferrous ion (Fe^{2+}, 750 versus 15 mg kg^{-1}) were also more enriched in human-disturbed streams than in forest streams ($p < 0.01$). Conductivity showed significant correlations with most sediment physicochemical properties, including pH, SOC, SN, Fe^{2+}, and S^{2-} ($p < 0.05$).

Previous studies have reported an association between increased water electrical conductivity and intensification of human activities (e.g., wastewater discharges and contaminated groundwater inputs) at local and even regional scales (Calvi et al. 2018; Kaushal et al. 2018). For example, studies have shown that increased effluent discharges from wastewater treatment plants in England led to higher electrical conductivity in river water (Schäfer et al. 2022). River conductivity has also been found to increase with the proportion of urban land cover (Que et al. 2023) and agricultural intensity (Atwell and Bouldin 2022) within catchments. Additionally, a previous study has documented a negative correlation between forest land cover and conductivity, while observing a positive association between agricultural and urban land cover and conductivity (Shupe 2017). These anthropogenic sources of stream water have higher conductivity and higher carbon and nutrient content

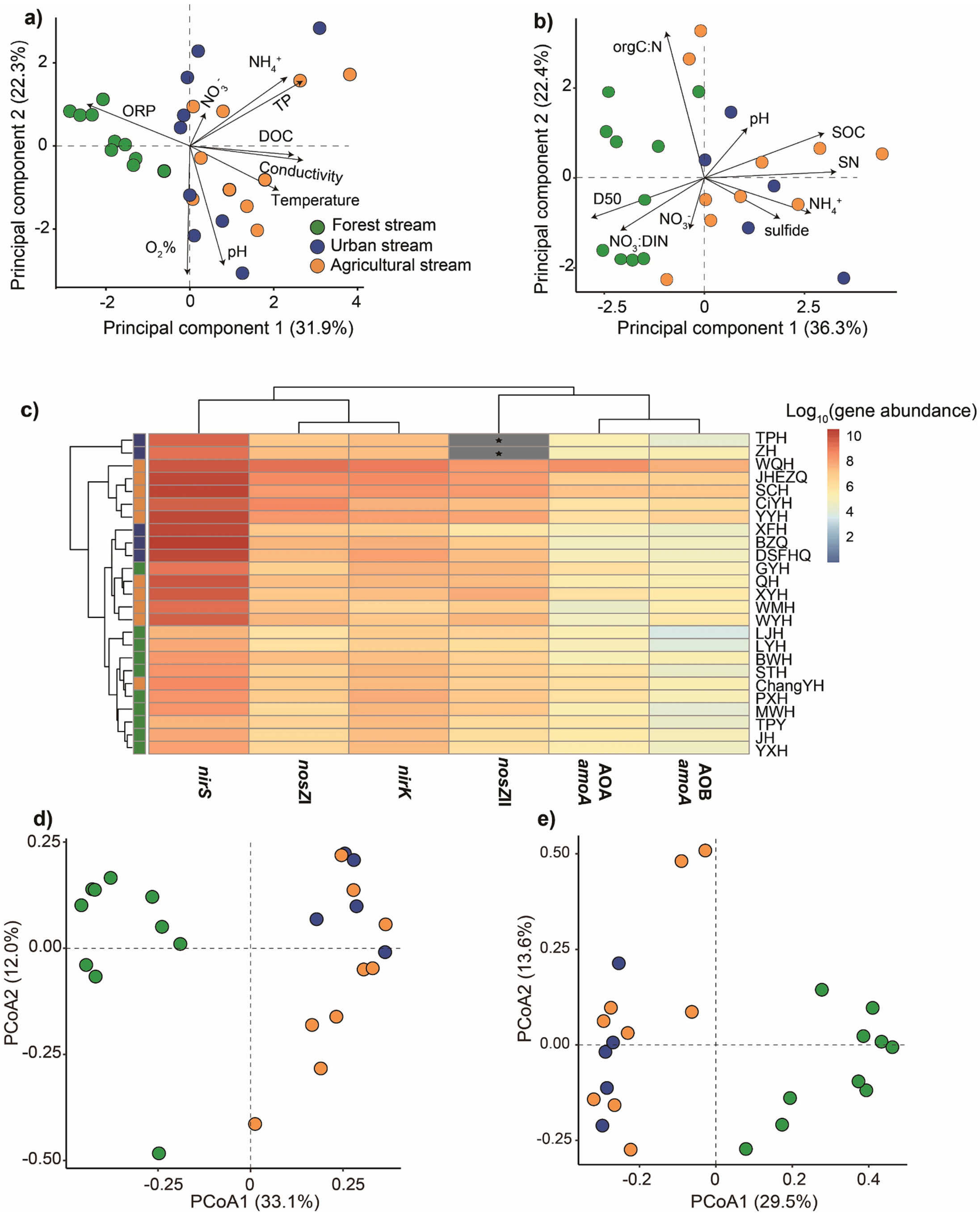

Fig. 2. Variations of stream water **(a)** and sediment **(b)** physiochemical properties, N_2O-related microbial functional profiles **(c)**, and *nirS*- **(d)** and *nirK*-type **(e)** denitrifying bacterial communities between different categories of streams. The symbol "☆" in **(c)** indicates that corresponding microbes were not detected.

compared to global averages (Herbert et al. 2015). Consequently, as conductivity increases, intensified human disturbance simultaneously introduces more carbon and nutrients into the adjacent streams. Furthermore, increased concentrations of Ca^{2+}, Na^{+}, and other cations under higher conductivity conditions would cause intensified NH_4^+-N desorption from sediment particles, resulting in elevated NH_4^+-N levels (Marton et al. 2012). For S^{2-} and Fe^{2+}, in addition to direct inputs (Zhang et al. 2023), the finer sediments, which consistently displayed higher conductivities in this study (Tables S3 and S4), may enhance the reduction of SO_4^{2-} and Fe^{3+}, contributing to the positive relationship between conductivity and S^{2-} and Fe^{2+} contents. Taken together, these results suggest that the synchronized changes in electrical conductivity and carbon and nutrient levels can be readily observed from pristine to human-disturbed streams.

3.2. Electrical conductivity as the best predictor of excess N_2O concertation (ΔN_2O)

In parallel with the physicochemical changes, the N_2O concentration, ΔN_2O, and N_2O flux varied markedly between forest and human-disturbed streams, but not between agricultural and urban streams (Fig. 3a-c). Dissolved N_2O concentrations fluctuated between 7.35 and 28.93 nmol/L, with an average of 11.5 nmol/L (n = 87 samples for 29 streams). The N_2O concentration in forest streams (9.76 ± 0.84 nmol N_2O L^{-1}, on average) was comparable to that in agricultural streams (10.73 ± 2.72), but significantly lower than that in urban streams

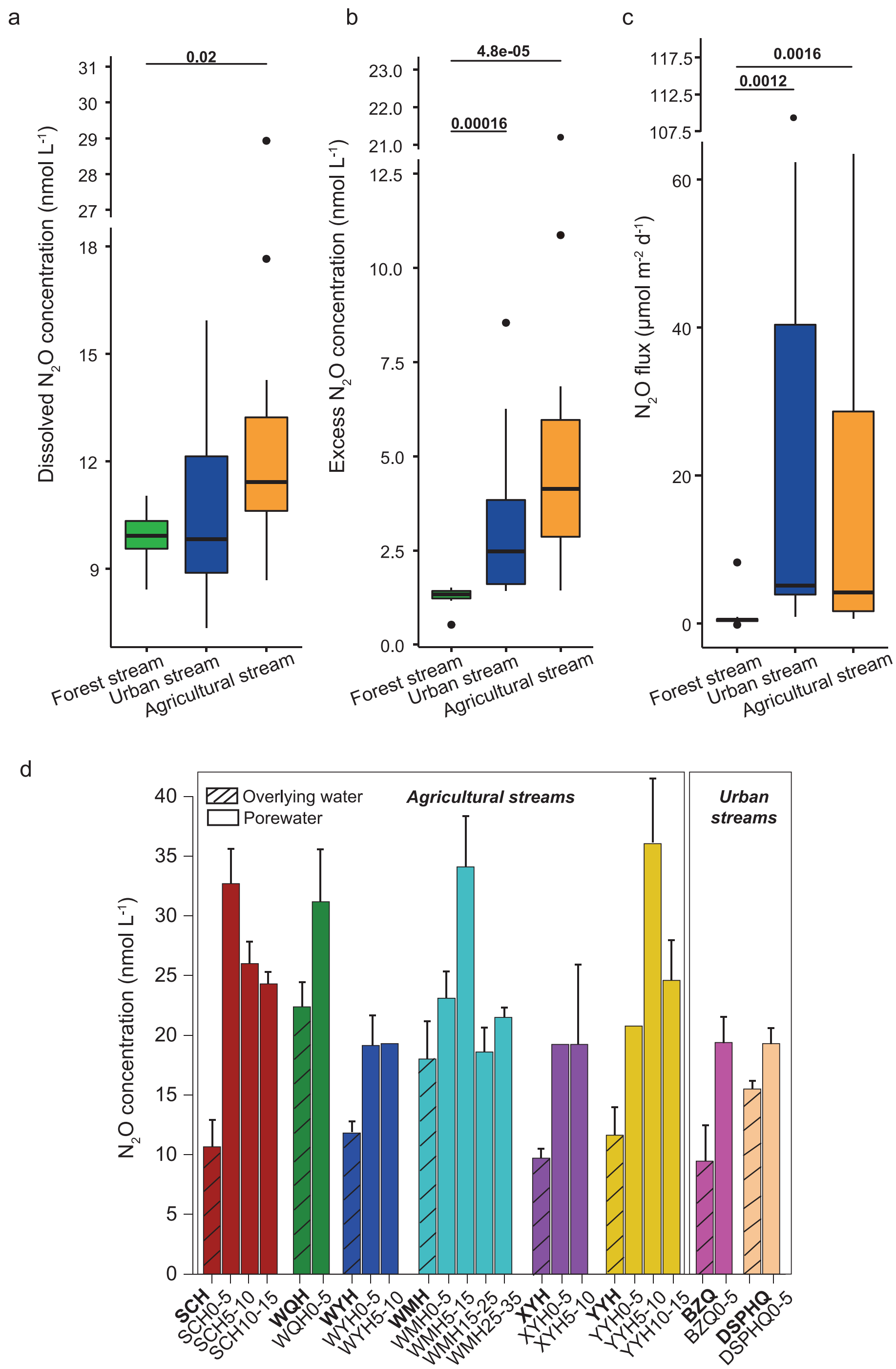

Fig. 3. Spatial variation of N_2O concentrations among different categories of streams **(a-c)** and across the depth profile **(**mean ± SD, **d)**. In panel (**d**), '0–5' denotes the porewater samples at sediment depths of 0–5 cm, followed by subsequent depth intervals in the sequence. Each sampling site is distinguished by a unique fill color.

(13.86 ± 5.78) (Fig. 3a, $p < 0.05$). Throughout the sampling period, all water samples were N_2O supersaturated and the ΔN_2O in both agricultural (6.36 ± 5.83 nmol N_2O L^{-1}, mean ± SD) and urban (3.51 ± 2.43) streams was significantly higher than that in forest streams (1.32 ± 0.35) ($p < 0.01$) (Fig. 3b). Accordingly, N_2O fluxes in agricultural (18.8 ± 26.6 μmol N_2O m^{-2} d^{-1}) and urban (26.1 ± 37.8) streams were significantly higher than those in forest streams (1.7 ± 2.8) ($p < 0.01$) (n = 58 samples for 29 streams, Fig. 3c). These results are consistent with previous studies (Hu et al. 2016), which report that human-disturbed streams emit N_2O more rapidly than pristine streams. These land use-induced changes in stream N_2O features align with the observed N_2O variation patterns in soil water, subsurface flow, and groundwater. In forest catchments, groundwater N_2O concentrations are generally lower than those in agricultural catchments, with the highest N_2O concentration in forest catchments being nearly 50 times lower than the respective measurement in agricultural catchments (Jurado et al. 2017). Similarly, the maximum N_2O concentrations in the soil water and subsurface flow within agricultural catchments are notably greater than those observed within forest catchments (Liu et al. 2022; Minamikawa et al. 2010).

The N_2O concentration in the available sediment porewater samples, all from urban and agricultural streams, was 1.6–3.2 times higher than that in the corresponding overlying water samples (Fig. 3d). The highest N_2O concentration in pore water was observed in the upper sediment layer (0–10 cm). This suggests that endogenous production of N_2O was an important source of N_2O emissions from these streams. Previous studies have also suggested that *in situ* production of N_2O in the hyporheic and benthic zones of streams is a major source of stream N_2O (Marzadri et al. 2017).

The results of correlation analysis and stepwise linear regression model showed that, among the multiple environmental variables assessed, conductivity and DIN were the two most important factors in indicating the variation in ΔN_2O (Fig. S1a-b and Fig. 4a-b), together accounting for 63 % of the variation in ΔN_2O. The positive association between ΔN_2O and DIN aligns with previous studies highlighting the importance of nitrogen availability in regulating N_2O concentrations and emissions (Marzadri et al. 2017; Wang et al. 2022). However, comparatively, the correlation between conductivity and ΔN_2O exhibited a stronger association than that between DIN and ΔN_2O ($r = 0.69$ versus $r = 0.45$, Fig. 4a-b), with conductivity as the primary predictor of ΔN_2O (Figure S1a-b).

Multiple recent studies have reported a significant positive relationship between conductivity and N_2O concentration (flux) in various river systems, including the catchments of Jialing River (He et al. 2017; Que et al. 2023), Yangtze River (Liang et al. 2023), and Chaohu Lake (Zhang et al. 2020). Furthermore, the dominant role of electrical conductivity in indicating the variability of N_2O concentrations has also been observed in several rivers, with R^2 values reaching up to 0.64 (Liang et al. 2023; Que et al. 2023). Upon reanalyzing the data regarding urban and forest streams in Beijing, we additionally discovered a significant increase in N_2O concentration with higher conductivities (Figure S2, n = 230). In the Haihe River catchment, which includes forested, cropland, and urban areas, conductivity showed a dominant influence on (excess) N_2O concentration in streams and rivers ($p < 0.05$, $r = 0.52$, unpublished data). These streams and rivers span diverse climatic zones and experience varying degrees of human disturbance. These consistent results hold great promise for the development of simple field-based assessments of riverine N_2O emissions using conductivity.

The concurrent effect of conductivity and DIN on ΔN_2O can be attributed to the uncoordinated changes between conductivity and water DIN from forest streams to human-disturbed streams. Different from conductivity, agricultural streams did not consistently contain higher DIN contents than forest streams (2.08 ± 2.00 versus 1.98 ± 1.25). This inconsistency may be partly because some contaminated groundwater in the agricultural zone experiences anoxic conditions and consequently has lower NO_3^- contents (Hu et al. 2016; Shupe 2017). Meanwhile, NH_4^+ concentration in stream water was positively correlated with conductivity (Spearman's $p = 0.002$). Additionally, several agricultural streams in our study area had undergone river bank protection with stone riprap, so that the riparian input of nitrate was negligible.

Another plausible explanation is that the increase in water electrical conductivity partly resulted from the extended contact time of river

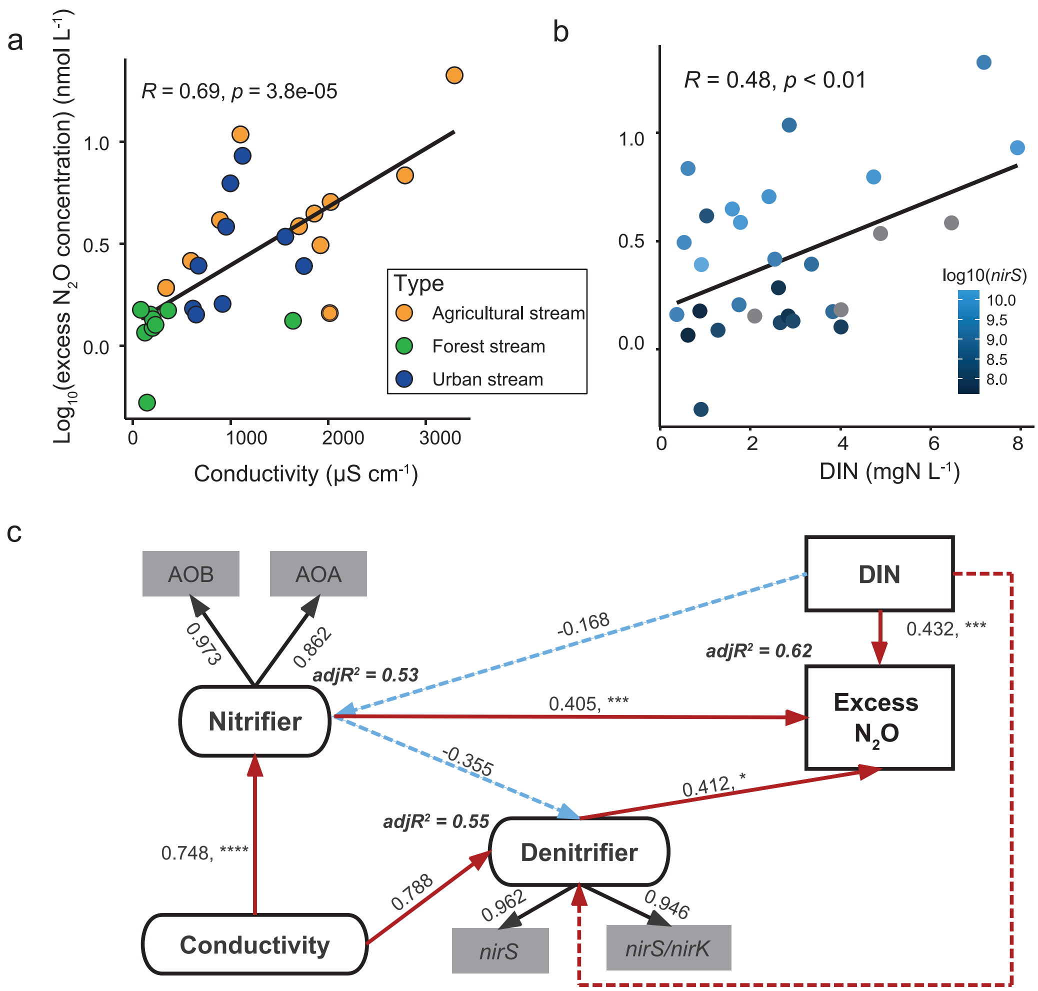

Fig. 4. Factors driving the spatial variations of ΔN_2O across different terrestrial land uses (**a-b**). The grey circles in **(b)** denote that no sediment sample was collected for the respective site. PLS model **(c)** depicting the effect pathways of environmental factors and microbial abundance on stream ΔN_2O.

water with surrounding reaction zones in both longitudinal and vertical directions (Cheng et al. 2020; Winnick 2021), which implies a greater degree and higher removal of NO_3^- (Winnick 2021). Among the three categories of streams, this phenomenon was expected to be more pronounced in agricultural systems characterized by lower flow velocities and silty sediments (Table S4). Given the significant positive relationship between conductivity and denitrification genes (see results below), we think that the latter explanation is more convincing. Previous research has reported that low-order rivers have a high nitrate removal capacity, with most N transported to these waters being rapidly processed before being transported downstream (Mulholland et al. 2008).

3.3. Significant correlation between conductivity and N_2O-related microbial functional profiles

Both hierarchical clustering analysis and RDA demonstrated that forest streams had distinct N_2O-related microbial functional profiles compared to human-disturbed streams (Fig. 2c). The abundances of both N_2O producers and N_2O reducers were significantly higher in human-disturbed streams compared to forest streams (Fig. 2c, $p < 0.05$). RDA analysis revealed that the variation in N_2O-related microbial groups between different land uses was mainly driven by total phosphorus and conductivity (Fig. 5a). However, the significant effect of conductivity on N_2O-related microbial abundance disappeared in the partial correlation analysis when excluding the effect of sediment carbon and nitrogen contents, which were positively correlated with all N_2O-related microbial abundances ($p < 0.05$). This suggests that the elevated carbon and nitrogen levels with increasing human disturbance partially contributed to the higher abundance of N_2O-related microbes in human-disturbed streams compared to forest streams.

However, the rates of increase in N_2O-related functional gene abundance along the conductivity gradient were significantly different. In particular, despite being considered functionally equivalent, the ratios of *nirS* and *nirK* were positively correlated with conductivity (Spearman's $p = 0.002$). The higher conductivities in human-disturbed streams on their own are, *per se*, a result of higher concentrations of soluble bedrock elements (Herbert et al. 2015; Kaushal et al. 2015). The higher concentrations of S^{2-} and Fe^{2+} under higher conductivity conditions in this study (Fig. 1b) might allow denitrifiers to utilize a wider range of alternative electron donors (Li et al. 2021), thereby increasing the *nir* abundance. This hypothesis was supported by the fact that the metabolic potentials of the higher-conductivity enriched denitrifiers in this study were associated with S^{2-} and Fe^{2+}, which was more evident for *nirS*-type denitrifiers compared to *nirK*-type denitrifiers (Table S5 and Table S6). Furthermore, the *nirS* to *nirK* ratio increased significantly with higher water temperatures ($p < 0.01$), corresponding to the higher temperatures under high-conductivity conditions. This is supported by a previous finding that only *nirS*-type denitrifiers were found to be temperature-sensitive under long-term organic and inorganic fertilization conditions (Cui et al. 2016).

Previous studies have reported that *nosZ* co-occurred more frequently with *nirS* than with *nirK* within denitrifiers (Hallin et al. 2018). Consequently, given the higher *nirS* to *nirK* ratio, denitrifiers with the genetic potential to perform complete denitrification were likely to be enriched under higher conductivity conditions. However, the *nir* to *nosZ* ratio, as well as the *nir* to *amoA* ratio, decreased significantly with

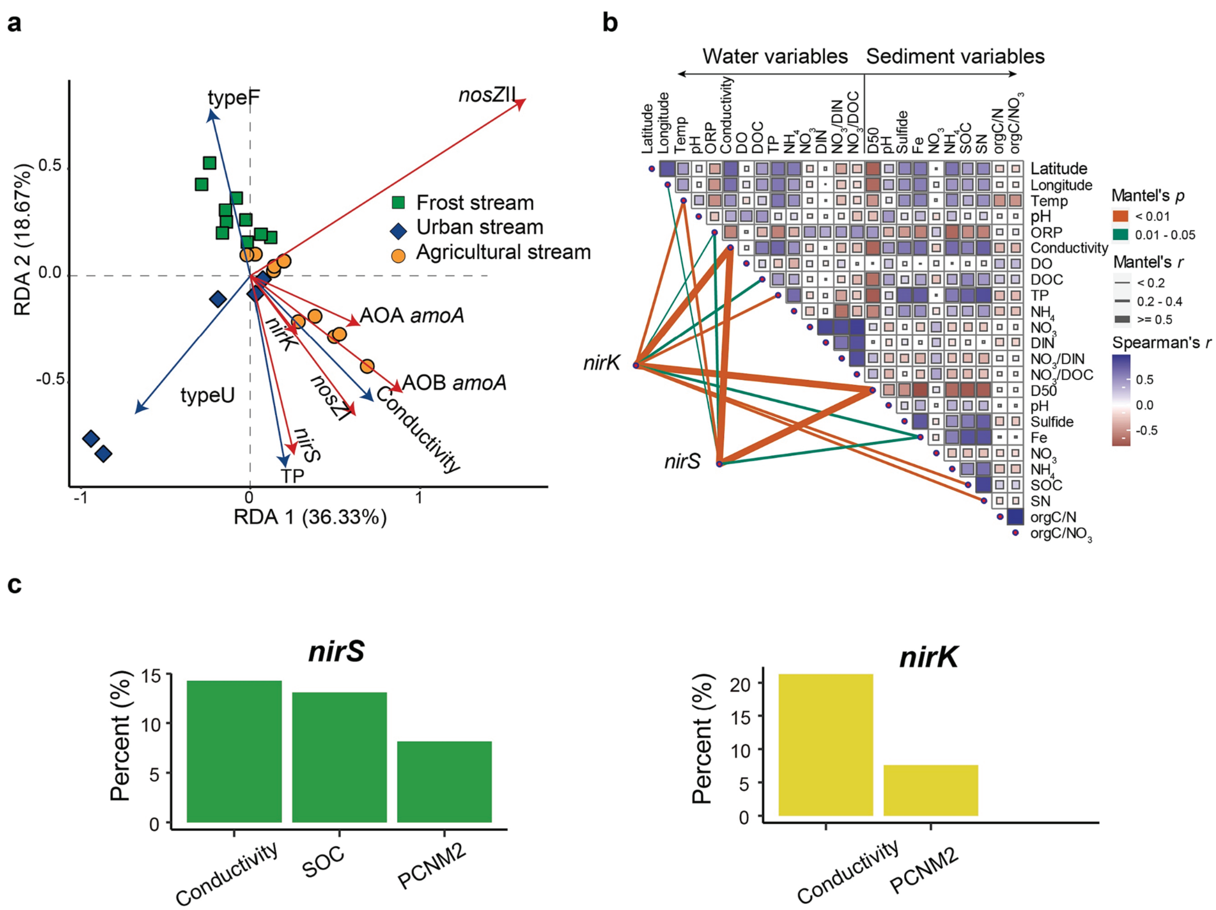

Fig. 5. Factors influencing the abundance and community structure of N_2O-related microbes. Redundancy analysis (RDA) revealed factors controlling the spatial variation of N_2O-related microbes **(a)**. Mantel correlations between physicochemical factors and denitrification communities **(b)**. Factors accounting for the spatial variation in denitrification community compositions **(c)**. PCNM2 represents a geographic distance-derived geospatial factor, which was calculated in the vegan package.

higher conductivity ($p < 0.01$). This discrepancy occurs because intensified human disturbance is generally accompanied by higher conductivities, sulfide, heavy metals, and toxic hydrocarbons are also enriched (Bissett et al. 2013). These pollutants are known to cause greater inactivation of the enzymes involved in N_2O reduction and nitrification than those responsible for denitrifier-mediated N_2O production (Bissett et al. 2013). In this study, we indeed found a dome-shaped variation in the abundance of the *nosZ* and *amoA* genes along the sulfide concentration gradient (Figure S3), while *nir* gene abundance consistently increased with sulfide concentration.

The increased abundance of genes related to N_2O production and the higher *nir* to *nosZ* ratio under high conductivity conditions were indicative of greater N_2O production and emission potential. This hypothesis was verified by a PLS pathway model, which exhibited good reliability and validity (composite reliability > 0.85; rho_A > 0.8; Cronbach's alpha > 0.8) and explained 62 % of the variance for ΔN_2O (Fig. 4c). This model suggests that the promotion of ΔN_2O under higher conductivity was partly due to the associated increase in the abundance of N_2O-producing nitrifiers and denitrifiers, driven primarily by the *nirS*-type denitrifiers (Fig. 4c). Furthermore, the contribution of denitrifiers in explaining the variance of ΔN_2O was greater than that of nitrifiers (0.42 vs. 0.25) (Fig. S1c), consistent with the higher *nir* to *amoA* ratios observed at higher conductivities, which corresponded to greater ΔN_2O ($p < 0.05$).

3.4. Dramatic changes in denitrification community with conductivity

Community structures of both *nirS*- and *nirK*-type denitrifiers demonstrated great differentiation between forest and human-disturbed streams, according to PCoA analysis and ANOSIM ($p < 0.05$) (Fig. 2e-f). Mantel test and rdaccahp analysis revealed that among the water and sediment physicochemical parameters, conductivity explained the most spatial variation in both the *nirS* and *nirK* communities, while the effect of DIN was minor and even negligible (Fig. 5b-c). TITAN analysis revealed that both *nirS* and *nirK* community compositions showed pronounced variations along the conductivity gradient (Fig. 6a-b). A conductivity of 500 μS cm^{-1} was identified as the predominant threshold point describing the variation in composition for both *nirS*- and *nirK*-containing denitrifying communities. Another threshold point was a conductivity of 1,600 μS cm^{-1}. Simultaneously, we found large variations in the ratios of ΔN_2O to conductivity across our study sites, with the largest ratios occurring within the conductivity range of 600–1,600 μS cm^{-1} (1.5×10^{-2}), followed in decreasing order by the range of > 1,600 μS cm^{-1} (9.0×10^{-3}) and < 600 μS cm^{-1} (2.9×10^{-3}) (Fig. 6c). These thresholds were in close proximity to those estimated for *nirS*- and *nirK*-type denitrification community transitions (500 and 1,600 μS cm^{-1}) (Fig. 6a-b). In contrast, the variations in *nirK* and *nirS* abundances along the conductivity gradient were distinct from those of ΔN_2O (Figure S4). This suggests that the compositional change of denitrifying bacterial community along the conductivity gradient is also important for influencing N_2O production and emission. Correspondingly, variance partitioning analysis revealed that the joint influence of environmental factors and denitrifier abundance only partially accounted for the variance in ΔN_2O, a value lower than that elucidated by the combined impact of environmental factors and denitrifier community (Fig. 6d-f).

On the other hand, increasing osmotic stress is an important pathway of freshwater salinization that affect microbial survival and growth (Herbert et al. 2015). The NCBI Blast results (Table S5 and Table S6) and the records in the Extremophiles Handbook (Horikoshi et al. 2010) indicated that halophilic or halotolerant denitrifiers were not present

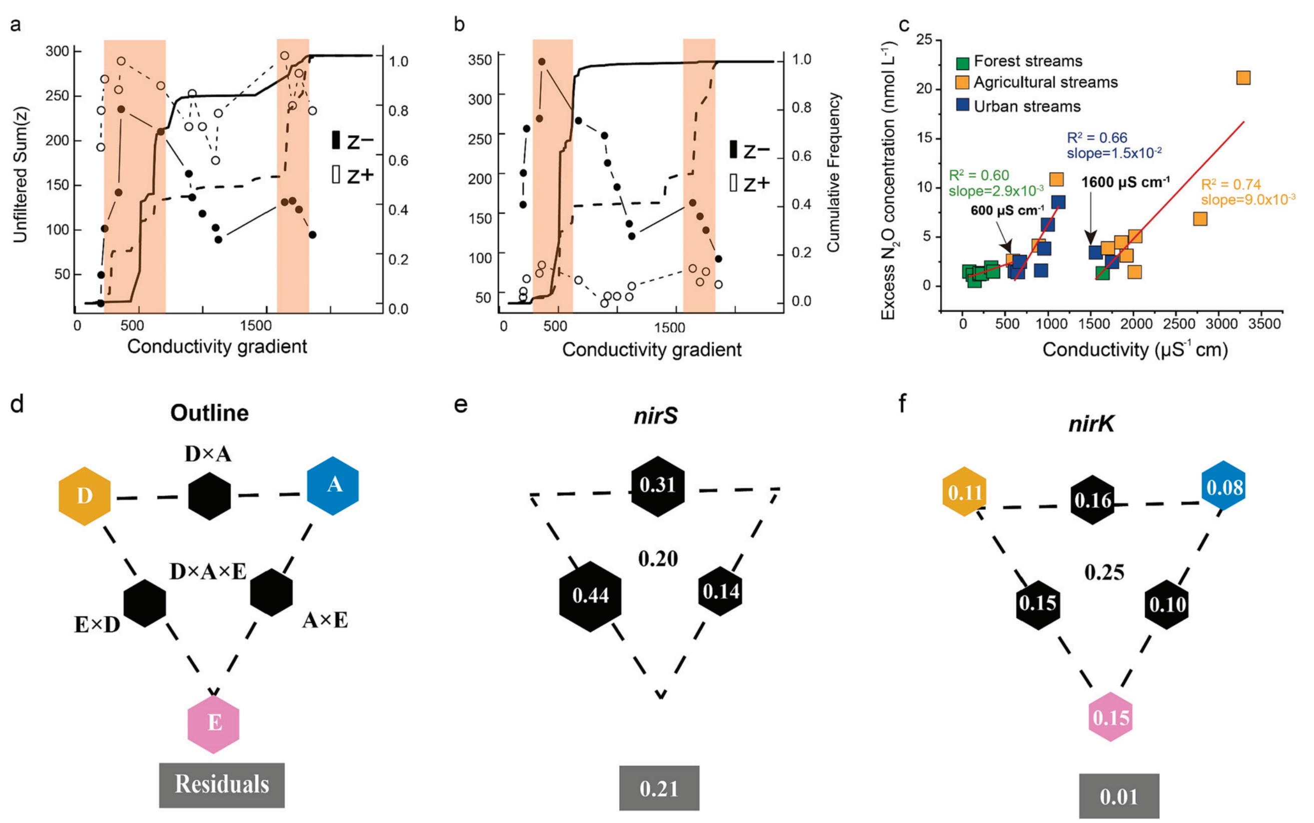

Fig. 6. Variations of nirS- (a) and nirK- (b) type denitrification community compositions and ΔN_2O (c) along the conductivity gradient. The variance of ΔN_2O was partitioned into environmental properties (S), the abundance of N_2O-producers and N_2O-reducers (A), the diversity of denitrification community (D), and by combinations of these factors (d-f). Detailed information is provided in Table S7. Geometric areas are proportional to the respective percentages of explained variation. The numbers in the hexagons denote the variation explained by each individual factor alone. Percentages of variation explained by interactions of two or all factors are indicated on the sides and in the middle of the triangles, respectively.

under higher conductivity conditions in the human-disturbed streams. In contrast, halophilic or halotolerant denitrifiers are common in high salinity estuaries (Magalhães et al. 2005). Thus, the N_2O-related microbes in our studied streams are expected to experience much lower osmotic stress than those in estuaries.

3.5. Increased exogenous N_2O inputs under higher conductivity conditions

The presence of exogenous N_2O inputs in these streams is expected, given the large terrestrial nutrient inputs they receive. Previous research has indicated that exogenous N_2O inputs are common in river systems, especially in lower-order rivers, to maintain baseline N_2O emissions (Zhang et al. 2022). Some studies have even found that wastewater treatment plant effluent, which is characterized by higher conductivity and N_2O levels, directly contributes to N_2O in certain streams (Que et al. 2023). In addition, contaminated groundwater, which often exhibits elevated conductivity and N_2O concentrations (Jurado et al. 2017), has been found to contribute to N_2O emissions from some agricultural streams and forest streams (Audet et al. 2020). Thus, there is a likely connection between stream conductivity and the magnitude of external N_2O inputs. This relationship is expected to be more pronounced in urban streams, where lateral N_2O inputs are limited. The relatively constant input of N_2O from sewage treatment plants, followed by dilution with downstream river water, may contribute to the positive relationship between conductivity and exogenous N_2O input.

Previous investigations have shown that baseflow water in natural streams has higher conductivity than runoff, with water conductivity being diluted as runoff increases (Carey et al. 2014). Pre-event water, on the other hand, displays intermediate conductivity values (Calvi et al. 2018). The different conductivities of these water sources suggest their different durations of contact with reaction zones in soils and/or sediments. Generally, baseflow water has longer contact times and thus potentially entrains more N_2O into streams and rivers. A similar pattern can be anticipated in the longitudinal direction, as a longer residence time within the river network provides more opportunities for stream water to accumulate ions and be influenced by exogenous N_2O inputs.

It is important to note that the salinity variation of surface water is influenced by some other factors, including the chemical composition of the underlying rock material (Calvi et al. 2018). This challenges our proposed positive relationship between electrical conductivity and exogenous N_2O inputs. It should be acknowledged that such a relationship is more applicable to individual streams and, at most, to streams of the same type. However, exogenous N_2O inputs should also be correlated with local nitrogen levels. Our incubation experiments demonstrated that without any nitrate addition, oligotrophic sediment samples (NO_3^--N < 0.45 mg kg^{-1}) emitted N_2O at lower rates, < 500 nmol N_2O d^{-1} kg^{-1} dry sediment, and behaved as N_2O sinks at higher N_2O concentrations (Figure S5), despite having higher conductivities. In contrast, sediment samples with NO_3^--N of 1.74 mg kg^{-1} emitted N_2O at rates of $>$ 8,000 nmol N_2O d^{-1} kg^{-1}. When additional NO_3^--N (3 mg/L) was added, simulating an overlying water NO_3^- supply, sediment samples emitted much higher amounts of N_2O (up to 16,320 nmol N_2O d^{-1} kg^{-1} dry sediment). Higher N_2O emission rates were observed in samples with higher conductivity and nitrate content. Forest streams generally have lower conductivity levels than agricultural and urban streams, and forested zones always have lower carbon and nitrogen levels than human-disturbed zones. Correspondingly, soil N_2O emission rates were higher in human-disturbed areas than in forest areas (Yin et al. 2022). Thus, electrical conductivity can provide some qualitative indication of the magnitude of exogenous N_2O input from forest streams to human-disturbed streams.

3.6. Mechanisms underlying the influence of electrical conductivity on excess N_2O concentration (ΔN_2O)

The current study unveiled the potential of electrical conductivity as an indicative parameter for assessing ΔN_2O across different types of land use, which was supported by an increasing number of reports of significant positive relationships between conductivity and (excess) N_2O concentration or flux (Liang et al. 2023; Que et al. 2023). The effects of electrical conductivity on stream ΔN_2O in our study area were intertwined with both endogenous N_2O production and exogenous N_2O input (Fig. 7). Human-disturbed streams receive elevated loads of carbon and nutrients in comparison to forest streams, coupled with the introduction of water possessing higher electrical conductivity and even higher temperature. This combination facilitated, in part, an increased production of N_2O, as evidenced by higher abundances of N_2O producers and increased net N_2O production potentials, consequently leading to higher ΔN_2O observed under high conductivity conditions. Beyond carbon and nitrogen, the elevated levels of ferrous iron and sulfide, concomitant with higher electrical conductivity, further contributed to the enhanced potential for net N_2O production.

The shifts in the denitrifier community from forest streams to human-disturbed streams with higher electrical conductivity were characterized by an enrichment of denitrifiers adapted to human disturbance, which also drove the increased N_2O production potential. Moreover, higher electrical conductivity is thought to be correlated with prolonged residence time of stream/soil water within surrounding reaction zones, affording microbes extended windows to produce N_2O. Furthermore, as previously discussed, electrical conductivity has shown promise in qualitatively indicating the extent of exogenous N_2O inputs across different land uses.

Among the endogenous pathways, the mechanisms by which salts themselves affect N_2O production and reduction in river systems have been poorly studied. This underscores the need for further research, particularly given the widespread and increasing reports of freshwater salinization (Cunillera-Montcusí et al. 2022). As global urbanization continues and agriculture expands, the electrical conductivity of stream water is expected to continue to rise (Kaushal et al. 2018). Therefore, it is crucial to investigate the universality of this relationship between stream (excess) N_2O concentration, or flux, and conductivity. If this relationship holds to be consistent, there will be an opportunity to develop simple field-based assessments of stream N_2O emissions across regional landscapes in both current and future scenarios.

4. Conclusions

This study revealed that electrical conductivity can serve as a reliable indicator of the effect of land use types on N_2O concentrations when exogenous inputs and endogenous production are considered together, with higher excess N_2O concentrations observed at higher conductivity. In addition to its coordinated growth with carbon and nutrient levels under increased human disturbance, electrical conductivity was correlated with changes in the N_2O-related microbial functional profile and community composition across different land use types. Furthermore, electrical conductivity had great potential in qualitatively indicating the magnitude of exogenous N_2O input across different land uses. Our findings hold promise for the development of simple field-based assessments of riverine N_2O emissions using electrical conductivity across regional landscapes. It is also important to explore the relationship between conductivity and carbon-based greenhouse gases, such as methane (CH_4) and carbon dioxide (CO_2). Investigating how conductivity correlates with the dynamics of these gases in streams and rivers will contribute to a more comprehensive understanding of the complex interactions between land use, electrical conductivity and other water chemistry, and greenhouse gas emissions.

CRediT authorship contribution statement

Sibo Zhang: Methodology, Investigation, Writing – original draft. **Xinghui Xia:** Conceptualization, Methodology, Writing – review & editing. **Yuan Xin:** Investigation, Formal analysis. **Xiaokang Li:**

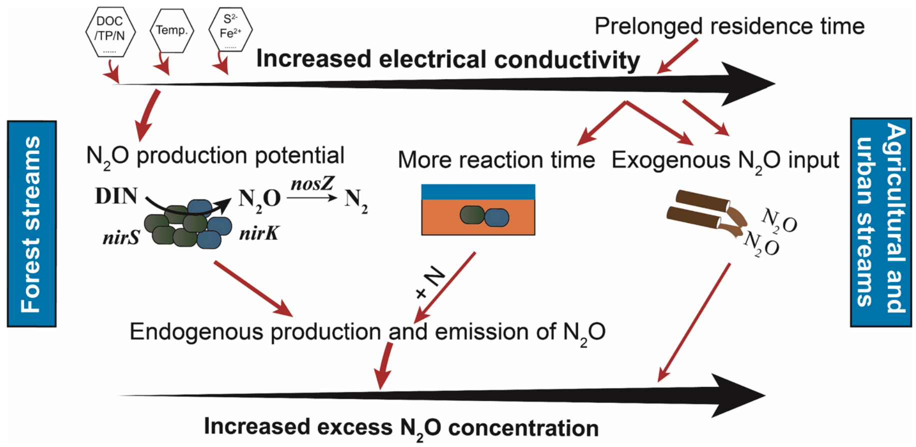

Fig. 7. Schematic showing of the underlying mechanisms for the significant roles of electrical conductivity in indicating variations in N_2O concentrations between forest streams and agricultural and urban streams. Red arrows indicate promotive effects. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Visualization, Formal analysis. **Junfeng Wang:** Formal analysis. **Leilei Yu:** Investigation, Software. **Cangbai Li:** Visualization. **William H. McDowell:** Writing – review & editing. **Qian Tan:** Writing – review & editing. **Zhifeng Yang:** Conceptualization, Project administration, Funding acquisition.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2023.130253.

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