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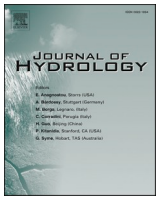

Research papers

# Unraveling the nexus: exploring river-groundwater interaction as the primary driver of eutrophication in river ecosystems

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ABSTRACT

Over recent decades, increased agricultural activities have significantly modified nitrogen (N) and water cycles, leading to a worsening of the environmental quality and widespread eutrophication. The present work investigates the critical issue of N contamination and its impact on eutrophication in three rivers located in the central part of the Po Plain (Northern Italy), one of Europe's hotspots of N-fertilizers input and loss to aquatic ecosystems. The primary scientific problem addressed is the role of river-groundwater interactions in exacerbating eutrophication, primarily driven by nitrate ($NO_3^-$). Historical data from the past ten years on dissolved inorganic N forms in groundwater and rivers were analyzed and interpreted in relation to different watershed managements. This analysis quantified both the volumetric and qualitative contributions of river-groundwater interactions to rivers eutrophication.

Results indicate that river-groundwater interactions can be indeed the main cause of eutrophication in intensively cultivated watersheds, with effects surpassing those of typical causes like wastewater. The study highlights how the simultaneous presence of inefficient irrigation practices promotes surface water (and groundwater) overexploitation, reducing dilution and increasing contamination. All the analyzed rivers showed localized increase in $NO_3$ concentration and worsening of their trophic status. Given the foresaw increase in groundwater and surface water use for irrigation under climate change pressures, this research provides a crucial empirical example of future challenges for regions with high N inputs and close relations among soil, groundwater, and surface water. The findings emphasize the urgent need for improved water and agricultural management to mitigate river-groundwater interaction-induced eutrophication.

## 1. Introduction

Nitrogen (N) is an essential element for agricultural productivity; however, its excessive input to ecosystems has led to global environmental concern. The N biogeochemical cycling has been unbalanced by anthropogenic activities, i.e. industrial N fixation. The widespread adoption of the Haber–Bosch process (1908) has enabled large-scale production and utilization of N fertilizers in agroecosystems, significantly increasing global agricultural productivity as well as N concentrations in aquatic ecosystems (Galloway et al., 2008, 2003; Smith et al., 1999), with far-reaching consequences as eutrophication, anoxia, loss of biodiversity and of valuable ecosystem functions and services (Tilman et al., 2001). Since the early 1990 s, the European Union has implemented several directives to contrast N contamination of surface water and groundwater, namely the Council Directive (91/676/EEC of 12 December, 1991), the Directive (2000), and the Directive (2006). In Europe, good chemical status has been achieved for 74 % of the groundwater, whereas this is not the case for almost 60 % of surface water bodies, that did not reach a good ecological status (European Environment Agency and Publications Office of the European Union, 2018; Nikolaidis et al., 2022). Hotspots of N pollution in surface waters have been identified in Denmark, Belgium, the Netherlands, and northern Italy (Grizzetti et al., 2021).

The Po Plain in northern Italy is considered one of the main N hotspots in Europe with respect to N inputs in agroecosystems (De Vries et al., 2022), diffuse N loss to aquatic ecosystems (De Vries et al., 2021),

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and $NH_3$ volatilization (Van Damme et al., 2022). The diffuse contamination and lack of regulation's efficacy were ascribed to several factors, as the accumulation of N in groundwater and soils (referred to as nitrogen legacy) (Ascott et al., 2017). Moreover, European regulations were not able to contrast site-specific irrigation practices that use large water volumes and affect N transport mechanisms (Pinardi et al., 2022). Due to Italy's failure to fully comply with the Nitrate Directive, in February 2023 the European Commission issued a reasoned opinion to Italy (INFR(2018)2249).

The Po Plain is characterized by a multilayer alluvial aquifer created by a series of gravels and sands with interbedded clay layers. The recharge zones for both the shallow and deep aquifers are situated in the foothills of the Alps (North) and the Apennines (South-West). Additionally, the phreatic aquifer receives substantial recharge from both direct precipitation and irrigation infiltration across the plain. Groundwater flows toward the Po River, from North to South in the prealpine area and from South to North near the Apennines (Sacchi et al., 2013).

In the Po Plain, studies on N dynamics at various scales reported that the co-occurrence of high N inputs and large water availability led to contamination problems in both surface and groundwater (Sacchi et al., 2013; Viaroli et al., 2013), resulting in eutrophication of riverine, deltaic, and coastal waters (Blaas and Kroeze, 2016; Viaroli et al., 2018). Nevertheless, the causes of this diffuse N contamination are not completely understood. The mechanisms underlying such contamination are facilitated by overfertilization and high permeability of soil and aquifer in the recharge zone (Laini et al., 2011; Martinelli et al., 2018; Sacchi et al., 2013). In these zones the aquifer acts as both N temporary sink, reservoir, and N supplier to surface waters via springs (Balestrini et al., 2021), along periods of months (Severini et al., 2022) to decades (i.e. nitrogen legacy, Basu et al., 2022). The spatial and temporal dynamics of N transfer across the soil-groundwater-surface water nexus are site-specific and poorly described. This prevents stakeholders and policymakers to provide effective best management practices (BMP) to contrast N contamination and improve the surface water chemical and biological quality.

In this context, the specific objective of this study is to explore the contribution of river-groundwater interactions to surface water N loads and eutrophication, shedding light on groundwater as overlooked pollution source. To this purpose, N budgets in three agricultural watersheds within the Po Plain, namely the Mincio, Chiese, and Mella, were contrasted to long-term patterns of inorganic N concentration in their groundwater and in the Mincio, Chiese and Mella rivers. The three watersheds are located within the same macro-region and share common features such as high density of farmed animals, resulting in high N inputs, high soil permeability, facilitating groundwater pollution, and areas characterized by river-groundwater interaction. However, they are characterized by different hydrologic regimes and surface and groundwater management practices, that may differently shape N transport mechanisms. We hypothesized for all watersheds a significant increase of inorganic N concentrations along the river courses, due to diffuse N inputs. We also hypothesized that a major N input results from the interaction between rivers and N-polluted groundwater. We speculate that the river-groundwater interaction could be converted from a problem to a solution if the N excess from fertilization is reduced in the future years and groundwater inputs could promote the dilution of point pollution sources such as wastewater treatment plants (WWTPs). Although this study was carried out in the Po Plain, its findings have implications beyond the study region, as shifts in river-groundwater interactions driven by climate change and agricultural practices are occurring in agricultural watersheds worldwide (Du et al., 2020; Hintze et al., 2020; Kwon et al., 2020; Ntona et al., 2022).

## 2. Material and methods

### 2.1. Study area

The watersheds of the Mincio, Chiese, and Mella rivers are located in the eastern portion of the Lombardy Region (Fig. 1). These rivers flow from North to South, from the Alps toward the Po River. The Mincio

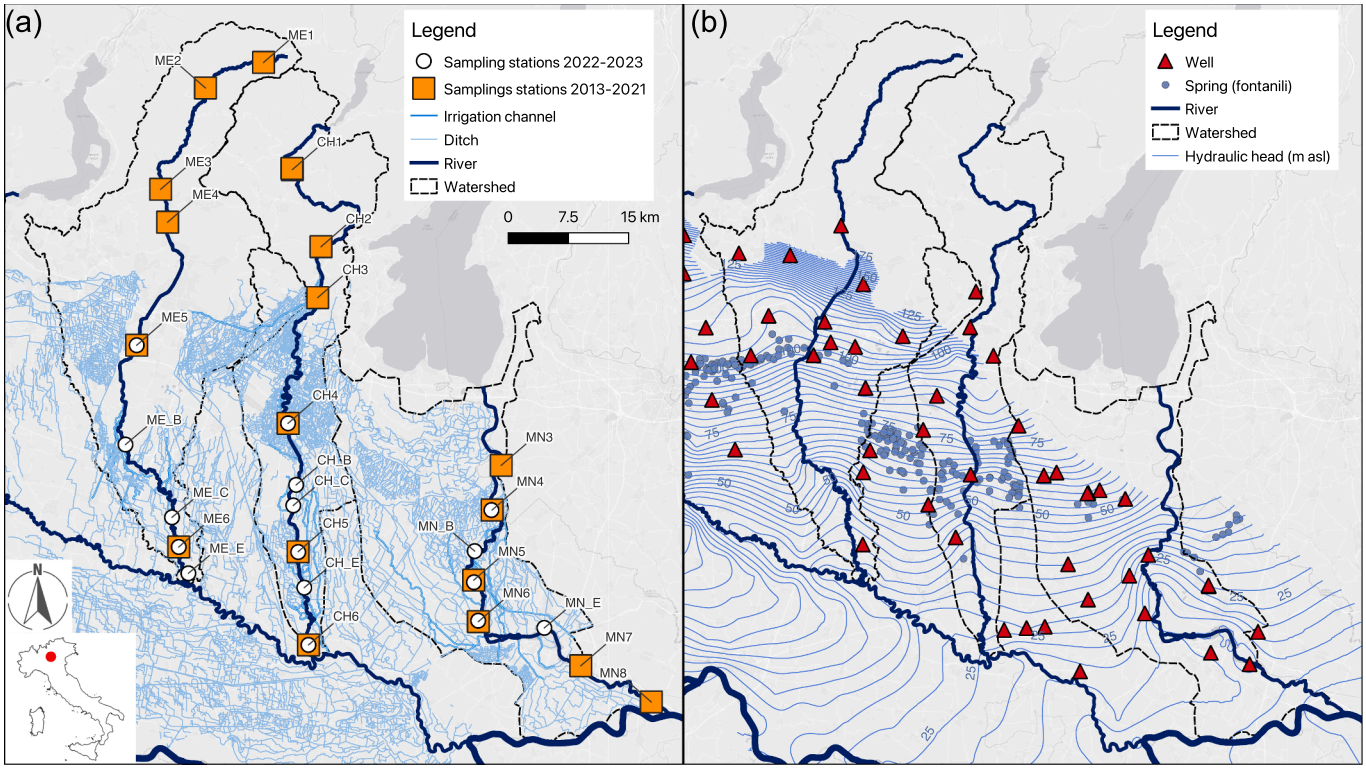


**Fig. 1.** (a) study area with the surface water sampling stations; (b) hydrogeological features with the wells used to characterize groundwater quality.

River is a tributary of the Po River, whereas the Chiese and Mella rivers flow into the Oglio River, which is a tributary of the Po River as well. The Mincio and Chiese rivers originate from alpine lakes, namely the Garda and Idro lakes, whereas the Mella River originates from the Maniva mountain area. The average annual discharge is 60, 36, and 11 $m^3s^{-1}$ for the Mincio, Chiese and Mella, and all three rivers are intensively used for irrigation during spring and summer. The three watersheds have already been investigated with respect to agricultural activities, nutrient budgets, biogeochemical cycles, and water chemistry (Pinardi et al., 2022, 2018; Racchetti et al., 2019; Severini et al., 2020; Soana et al., 2011). They host high densities of swine and cattle, resulting in a considerable N surplus according to soil system budget approach in the watersheds, mainly due to the over-application of manure as fertilizer (Viaroli et al., 2018).

The watersheds belong to the multilayer alluvial aquifer of the Po Plain, one of the largest aquifers in Europe (Perego et al., 2012), and 60 % of the utilized agricultural area (UAA) is classified as a nitrate vulnerable zone (NVZ), following the Nitrate Directive. In the Po River watershed, the recharge areas are located near the mountain areas (Alps and Apennines), from where groundwater flows toward the Po River (Martinelli et al., 2018). The recharge area (high plain) is composed by pebbles, gravel, and sand, with silt and clay as less permeable layers (Fig. A2).

The aquifer becomes semi-confined and confined in the proximity of the Po River (low plain), where it is mainly composed of sand, silt, and clay (Martinelli et al., 2018; Rotiroti et al., 2021). The decrease in the hydraulic gradient favors the emergence of a large number of lowland springs, locally called “fontanili” (Fig. 1b). The agricultural fields above the unconfined aquifer are intensively irrigated mainly through flood irrigation (also known as surface or furrow irrigation) (Pinardi et al., 2022; Rotiroti et al., 2019; Soana et al., 2011). This is the least sustainable and efficient irrigation method due to its low uptake efficiency and constitutes the main recharge mechanism of the aquifer (Rotiroti et al., 2019; Severini et al., 2022). The water for irrigation is mainly derived from the river in the Mincio watershed (Pinardi et al., 2022) whereas in the Chiese watershed, the river provides a minor fraction of the total water used, which is mainly retrieved from the aquifer, through irrigation wells (Severini et al., 2023). In the Mella watershed, both groundwater (from wells) and surface water (from the Mella River) are used (Zanotti et al., 2019).

In the three watersheds, $NO_3^-$ concentration in the high plain may exceed the national drinking water threshold (50 mg $NO_3^-$ $L^{-1}$), and vary in time and space depending on the groundwater flow path and aquifer recharge. In the lower plain, given the chemically reduced conditions, N is generally found as ammonium ($NH_4^+$), with concentrations that may exceed the national limit of 500 μg $NH_4^+$ $L^{-1}$ for drinking purposes. $NH_4^+$ in the low plain is generated by the degradation of organic matter in localized deposits of peat within the clay and silt aquitards (Rotiroti et al., 2021). The peats originated from abandoned meanders of the ancient Po River and its tributaries which were subsequently buried by younger alluvium (Miola et al., 2006).

### 2.2. Aquifer characterization

The conceptual model of the aquifer was created using 61 lithological logs of boreholes downloaded from the Lombardy Region dataset (https://www.geoportale.regione.lombardia.it/en-GB/home, accessed on 13 December 2023). From these data, 5 lithological cross-sections were created, three oriented N-S along the river courses and two oriented W–E in the higher and lower plain. Sediments were classified as pebble, conglomerate, gravel, sand, peat, and silt and clay. Water table data at regional scale, created in 2014, was downloaded from the Lombardy Region dataset (https://www.geoportale.regione.lombardia.it/en-GB/home, accessed on 13 December 2023). Groundwater heads trend between aquifer recharge and decline periods were derived from Rotiroti et al., (2019) for the Mella watershed and from Severini et al., (2022) for the Mincio watershed. Groundwater heads data in six shallow wells in the Chiese watersheds (Fig. A1) were used to characterize recharge and depletion dynamics of groundwater beneath it. Their altitudes (m a.s.l.) were obtained from the national Lidar dataset (±15 cm altimetric accuracy and ± 30 cm planimetric accuracy), as well as for riverbeds altitudes.

### 2.3. River and groundwater data

Historical data on dissolved inorganic N ($NO_3^-$, $NO_2^-$, and $NH_4^+$) concentration in the rivers (from 2015 to 2021) and the surrounding aquifer (from 2013 to 2021) were downloaded from the Lombardy Regional Environmental Protection Agency (ARPA Lombardia – https://www.arpalombardia.it, accessed 07 November 2023). From the same dataset, major ions concentration, pH, temperature, and electrical conductivity (EC) of groundwater were downloaded for the same period and used to create Piper plots and ionic ratios biplots of groundwater chemistry. The sampling stations are reported in Fig. 1a, b. When present, samples with concentration below the detection limit (DL) were reported as 0.5 × DL. To better characterize the area of river-groundwater interaction, a more detailed sampling was performed in 2022 (for the Mincio River and Chiese River) and 2023 (for all three rivers). The samplings were carried out at least seasonally for a total of 68 samplings, with many of them concentrated during the crops' irrigation period (April-September). $NO_3^-$, $NO_2^-$, and $NH_4^+$ concentrations were measured spectrophotometrically according to A.P.H.A. (1981). Briefly, $NH_4^+$ was determined using salicylate and hypochlorite in the presence of sodium nitroprussiate, $NO_2^-$ was determined using sulphanilamide and N-(1-naphtyl)ethylen-diamine, and $NO_3^-$ was determined using the salicylate method.

River-groundwater interaction was assessed through changes in river chemistry and discharge. Starting from the potentiometric map reconstructed in 2014, ad-hoc sampling stations were identified to characterize groundwater inputs during 2022–2023. The river discharge was measured using a standard configuration StreamPro ADCP (Teledyne RDI Instruments). Discharge data were elaborated using the software WinRiver II (version 2.24). The discharge in every section was calculated as the average of at least four measurements with a relative standard deviation < 5 %.

The R software (R Core Team, 2022) was used for the statistical tests. The package lme4 (Bates et al., 2015) was used to perform linear mixed effect analyses of the relationship between i) $NO_3^-$ concentration in rivers and the groundwater input, ii) the differences in $NO_3^-$ concentration between irrigation and non-irrigation periods, and iii) the increase in N:P molar ratios due to groundwater inputs. To cope with non-normality, a box-cox transformation was applied to the data. The areas of groundwater input and the irrigation phase were used as fixed effects in two separate models, whereas the sampling stations were used as random effect to deal with the dependence of the samples along the river stretches.

The analysis was performed using only $NO_3^-$ concentrations since nitrate is the most abundant N form in the studied watersheds, a

**Table 1**
LIMeco thresholds.

| | Threshold | | | | |
|---|---|---|---|---|---|
| | High | Good | Sufficient | Poor | Bad |
| 100-DO (%) | ≤\|10\| | ≤\|20\| | ≤\|40\| | ≤\|80\| | >\|80\| |
| NH4 (mg/L) | ≤0.04 | ≤0.08 | ≤0.16 | ≤0.31 | >0.31 |
| NO3 (mg/L) | ≤2.7 | ≤5.3 | ≤10.6 | ≤21.3 | >21.3 |
| Total-P (μg $L^{-1}$) | ≤50 | ≤100 | ≤200 | ≤400 | >400 |
| Score | 1 | 0.5 | 0.25 | 0.125 | 0 |
| Final LIMeco score | ≥0.66 | ≥0.50 | ≥0.33 | ≥0.17 | < 0.17 |

common feature of the Po Plain (Pinardi et al., 2018; Soana et al., 2011) and other agriculture-dominated watersheds (Hill, 2023; Li et al., 2023). Non-parametric tests (Mann-Kendall and Sens's slope) were used to detect significant trends in N forms ($NH_4^+$, $NO_2^-$, $NO_3^-$) in rivers and groundwater with the package mkac (Butler, 2019), adjusting the p-value if data autocorrelation was found. The Mann-Kendall test (Kendall, 1948; Mann, 1945) is a statistical method used to determine if there is a consistent trend in a variable over time, either increasing or decreasing, and not necessarily following a linear pattern. To assess if the trend is positive or negative, the Sen's estimator of slope has been preferred to a simple slope from a linear trend since it is very robust against outliers (Sen, 1968). To characterize the eutrophication level, the LIMeco index (Macro-descriptors Pollution Level for the Ecological Status) was applied to the three rivers for the period 2015–2021. LIMeco is the index proposed by the Italian law (D. Lgs. 152, 2006) to characterize the trophic level using dissolved oxygen (DO), $NH_4^+$, $NO_3^-$, and total phosphorus (P) following the WFD (Erba et al., 2022). In riverine ecosystems, differently from lakes, nutrient levels better than chlorophyll concentration are proxies of eutrophication. Indeed, the development of planktonic communities can be inhibited in turbulent waters despite high nutrient levels.

The LIMeco scores are assigned to each parameter following the thresholds outlined in Table 1. For consistency, original N forms in the index were converted from N-NH4 and N-NO3 to $NH_4^+$ and $NO_3^-$, respectively. The classification of water quality relies on the average scores of the four parameters and leads to a final quality class for the considered sampling stations. It must be highlighted how, for surface waters, the maximum tolerable $NO_3^-$ concentration is 21.3 mg $NO3^-$ $L^{-1}$. This limit is significantly lower than that admissible for groundwater, which is considered polluted if the concentration exceeds 50 mg NO3 $L^{-1}$. Thresholds for $NH_4$ + are 0.3 mg $NH4^+$ $L^{-1}$ in surface waters and 0.5 mg $NH4^+$ $L^{-1}$ in groundwater.

### 2.4. Calculation of soil system budget

Changes in N loads from diffuse agricultural sources in the three watersheds were assessed by collecting census data over the last two decades and computing a comprehensive input–output N budget across the UAA. The soil system budget (SSB) was calculated as the net difference between inputs (livestock manure, synthetic fertilizers, biological N-fixation, atmospheric deposition) and outputs terms (crop harvest, ammonia volatilization, and denitrification in soils), following the approach previously tested and applied to several tributaries of the Po basin, including in particular rivers in the Lombardy Region (Musacchio et al., 2021; Pinardi et al., 2018; Racchetti et al., 2019; Soana et al., 2011).

Nitrogen balances in agricultural soils were compiled for the years 2000 (pre-WFD), 2010, 2014, and 2020. See Supplementary Material for details of calculation methods, sources of census data, and agronomic coefficients.

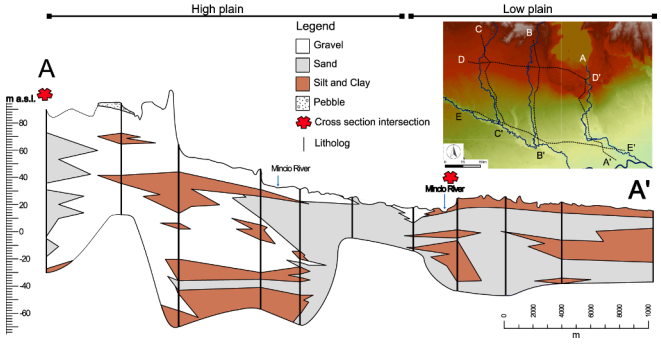


**Fig. 2.** Lithological cross-section AA' along the Mincio River.

## 3. Results

### 3.1. Analysis of river-groundwater interaction dynamics

The reconstruction of the aquifer setting allowed the identification of unconfined (northern part) and confined portions (southern part) of the aquifer in the investigated watersheds. An example of the setting is reported in Fig. 2 with the lithological cross-section along the Mincio River, whereas the other cross-sections are reported in the Supplementary Material (Fig. A2).

In the six wells used to characterize the groundwater level in the Chiese watershed, where previous groundwater data were not available, the variation was ± 1.2 m during 2023, with lower levels during summer, i.e. the irrigation period. The groundwater heads were always above the river level (Fig. A1). The hydraulic gradient averaged 0.003 ± 0.001 (mean ± standard deviation) and was N-S oriented and toward the Chiese River in the central portion.

River-groundwater interaction was assessed through changes in river flow, which are summarized in Table A1. In general, the areas of flow increase due to groundwater inputs are consistent with the potentiometric map of 2014 (Fig. 1b). In some sectors of the rivers, the interaction with groundwater is localized slightly upstream or downstream the location hypothesized by the potentiometric map. However, such differences are part of the approximation given by the regional scale of the original potentiometric map, much larger than the portion presented in Fig. 1b. The Mincio River has a higher groundwater input during the irrigation period and its mainly located between the stations MN_B and MN6 (Fig. 1a). The Chiese River has higher groundwater inputs during autumn and winter, far from the irrigation period and constituting a significant percentage of the total flow. The river-groundwater interaction is located between the stations CH5 and CH6. The Mella River has a groundwater input that follows a seasonal pattern as the Chiese River. The overall groundwater input to the Mella River is the highest among the investigated rivers, it is more influential during autumn and winter and is located between the stations ME_B and ME_E. During summer, the input of groundwater was 186 % of the river flow because the river was let dry by irrigation channels diverting its water. At the same time, the Mella River consistently gained groundwater producing a significant flow a few km downstream. As part of this flow was also used for irrigation, the discharge at the closing section was much lower than the total groundwater input.

### 3.2. Hydrochemical characterization of groundwater and surface river water

The most recent groundwater data (2021) were plotted in a Piper diagram (Fig. 4) and are summarized in Table A2. The Piper diagram was created for 2021 due to the constant hydrochemistry of groundwater during the investigated period (see Section 3.3). The distribution of data was used to identify hydrochemical differences among groundwater from the hill portion, high plain, and low plain areas of the watershed. Wells were grouped according to their distance from the Alps (hill < high plain < low plain) and the confined-unconfined condition of the aquifer. In all samples, the calcium-bicarbonate water type prevails, with very similar chemical properties among samples. The spatial variability of the groundwater samples in the Piper diagram can be attributed mostly to bicarbonates ($HCO_3^-$), with an increased concentration from the recharge area (hill-high plain) to the confined aquifer (low plain). Compared to the wells within the Mella and Mincio watersheds, those in the Chiese watershed look slightly less mineralized. Surface waters also fall within the calcium-bicarbonate water type (Fig. 4b), with an increased $HCO_3^-$ concentration from upstream to downstream the river-groundwater interaction area. Almost all samples display a $Ca^{2+}$+$Mg^{2+}$ excess over $HCO_3^-$+$SO_4^{2-}$ (Fig. A3a). Moreover, most of the samples in the $Ca^{2+}$/$HCO_3^-$ biplot fall above the 1:2 ratio (Fig. A3b).

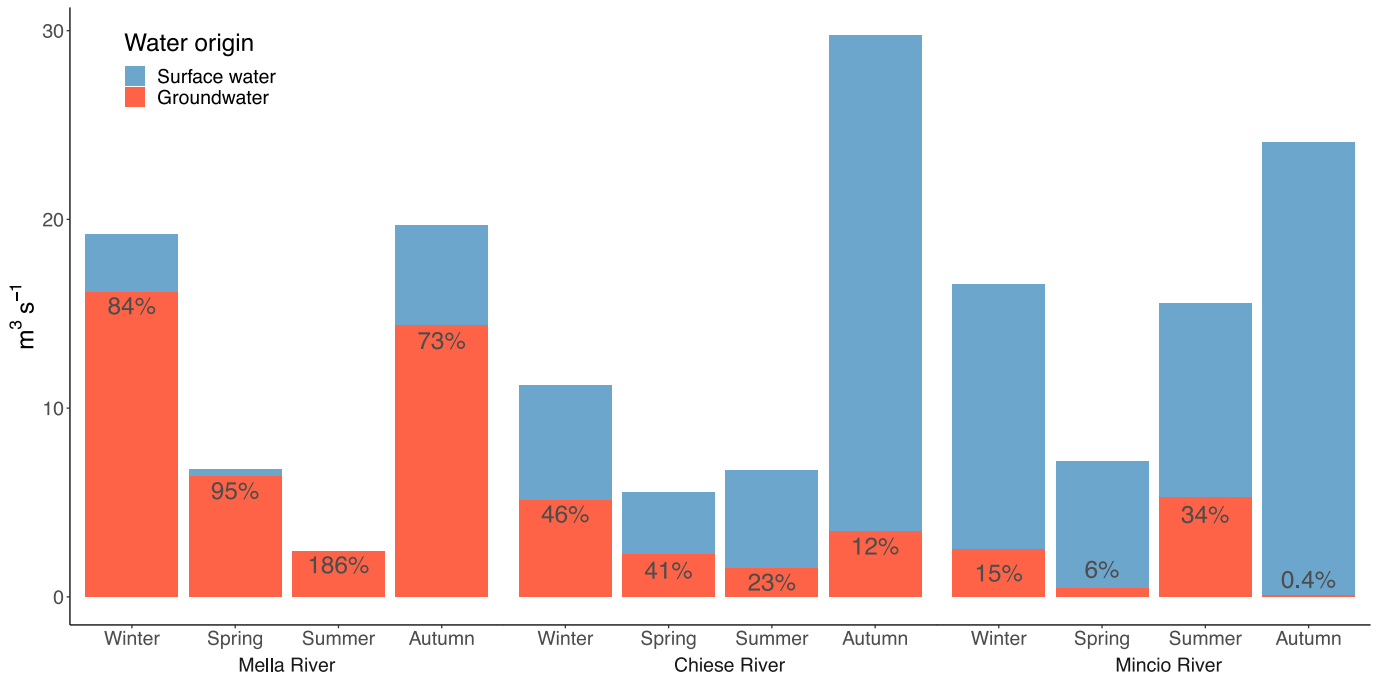


**Fig. 3.** Groundwater input to the investigated rivers. The bars represent the flow measured downstream the river-groundwater interaction area. The red portion represents the percentage of groundwater contribution to total flow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

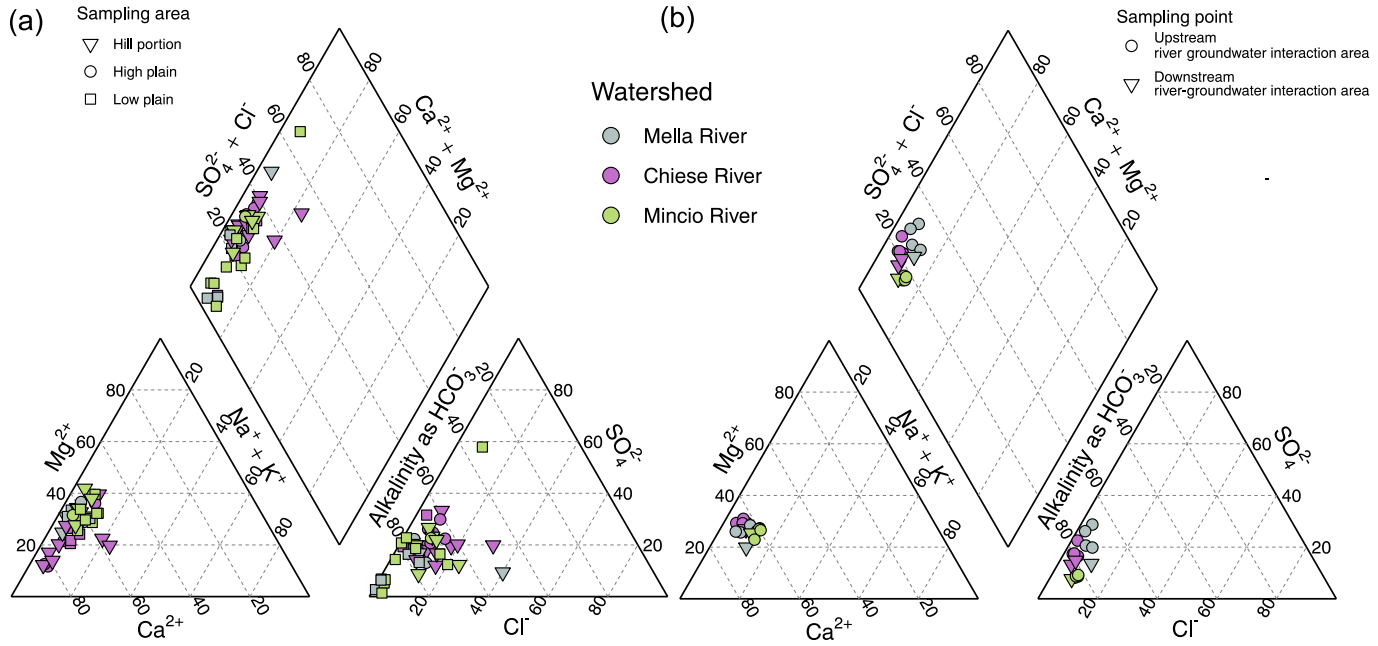


**Fig. 4.** Piper diagrams showing the chemical composition of the groundwater (a) and surface water samples (b) in the investigated watersheds.

### *3.3. Evaluation of nitrogen contamination in the Mincio, Chiese and Mella rivers*

$NH_4^+$ concentrations in groundwater are usually low in the recharge area (averaging 57 μg $NH_4^+$ $L^{-1}$ in the hill portion and 110 μg $NH_4^+$ $L^{-1}$ in the high plain), whereas they increase significantly in the low plain area (averaging 672 μg $NH_4^+$ $L^{-1}$), above the pollution threshold of 500 μg $NH_4^+$ $L^{-1}$ for drinking purposes (Fig. 5c). This trend aligns with groundwater redox and dissolved oxygen, decreasing from the high to the low plain. The Mann-Kendall estimator reported a statistically significant (p-value $< 0.05$) temporal trend of concentrations in the hill area and high plain. The trend was characterized as decreasing, with the Sen's slope equal to $-0.69$ and $-0.73$, respectively. In the low plain, no significant temporal trend of $NH_4^+$ concentration was detected. The full output of trend analysis in groundwater is reported in Table A3. The spatial trends of $NO_3^-$ concentration are opposite to those of $NH_4^+$, with lowest values in the low plain and peaks is in the recharge area (Fig. 5a, b). Here, the maximum measured concentration was 104 mg $NO_3^-$ $L^{-1}$ (2015), and many data exceed 50 mg $NO_3^-$ $L^{-1}$, the limit imposed by both Water Framework Directive (2000/60/EC) and Nitrate Directive (91/676/

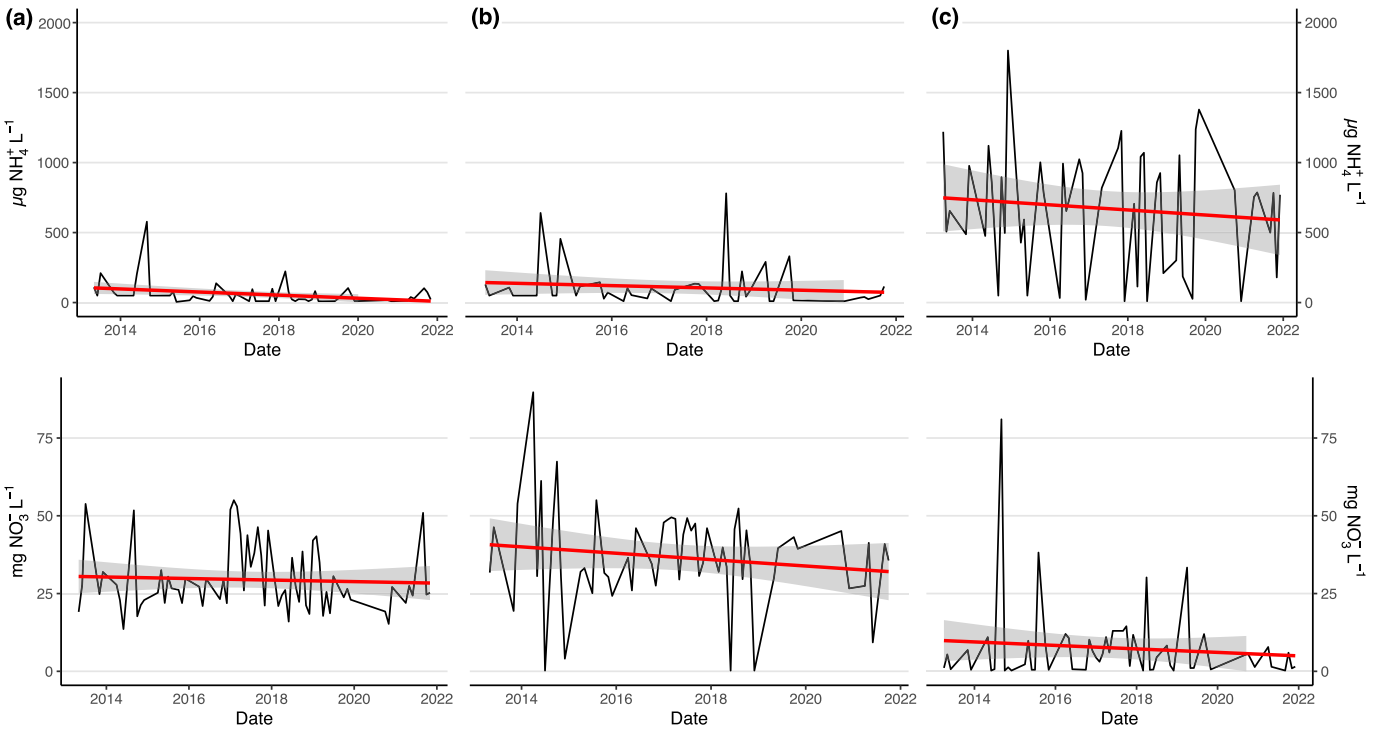


**Fig. 5.** $NH_4^+$ and $NO_3^-$ concentration in groundwater from the hill area (a), high plain (b), and low plain (c).

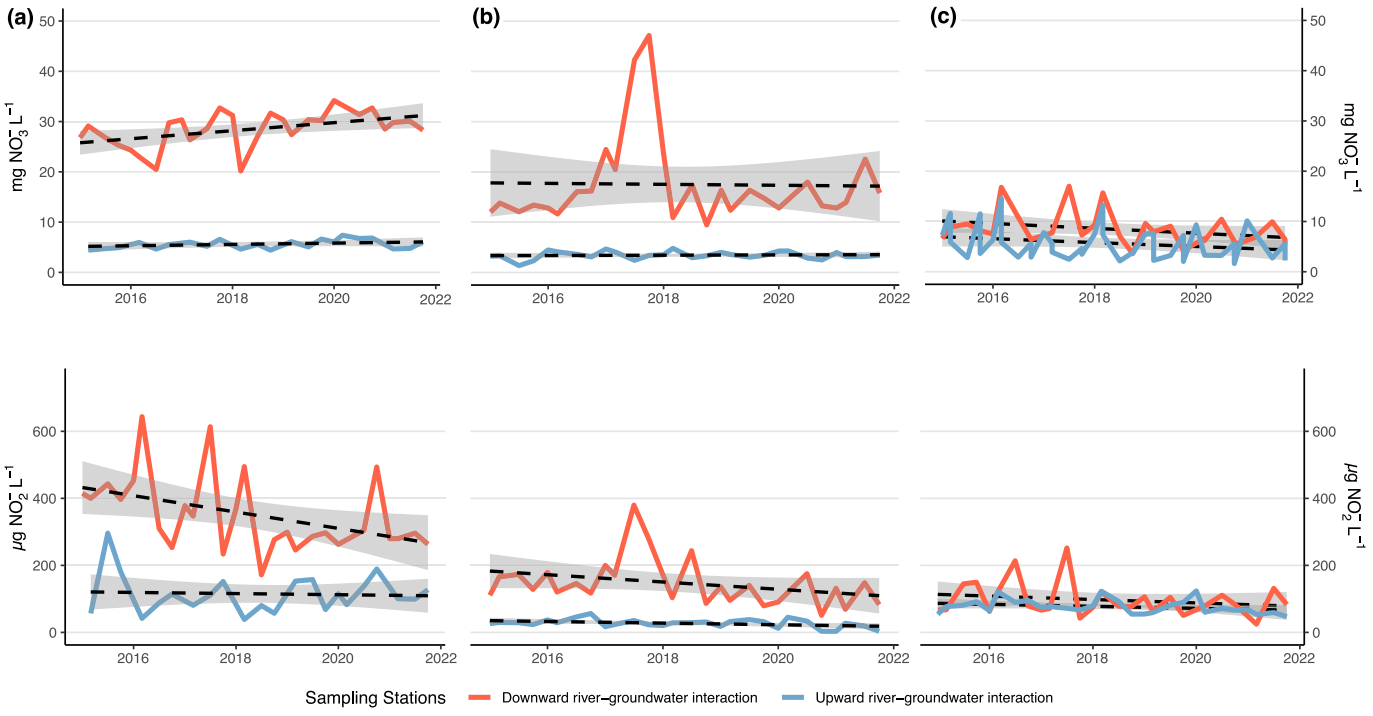


**Fig. 6.** $NO_3^-$ and $NO_2^-$ concentration in the Mella (a), Chiese (b), and Mincio (c) rivers upward and downward the river-groundwater interaction area.

EEC). The average $NO_3^-$ concentration in the hill portion is 29.45 mg $NO_3^-$ $L^{-1}$, whereas in the high plain it rises to 36.61 mg $NO_3^-$ $L^{-1}$ and decreases to 7.56 mg $NO_3^-$ $L^{-1}$ in the lower plain.. The Mann-Kendall and Sen's slope estimator tests did not highlight significant trends due to the almost constant $NO_3^-$ concentration in all the sub-areas. $NO_2^-$ concentration is usually low; no differences among the three areas and no temporal trends were detected (Fig. A4).

The trends of $NH_4^+$, $NO_2^-$, and $NO_3^-$ concentrations were also tested in surface waters, differentiating between samples inside or outside of the river-groundwater interaction area (Fig. 6). The results from Mann-Kendall and Sen's slope estimator tests were heterogeneous among the three rivers. The Mincio River was characterized by a stable $NH_4^+$, $NO_2^-$, and $NO_3^-$ concentration during the investigated period. Only upstream the groundwater input, $NO_2^-$ concentration showed a statistically significant decrease through time (p-value $< 0.05$, Sens's slope $= -0.0002$). In the Chiese River, the concentration of $NH_4^+$ was

characterized by a decreasing trend downstream the groundwater input (p-value < 0.05, Sens's slope = − 0.002), whereas $NO_2^-$ concentration decreased through time both upstream (p-value < 0.05, Sens's slope = − 0.0001) and downstream (p-value < 0.05, Sens's slope = − 0.0007) the river-groundwater interaction area. As in the Mincio River, $NO_3^-$ concentration remained stable through time. In the Mella River, $NH_4^+$ concentration remained stable through time, whereas $NO_2^-$ values decreased downstream the groundwater input area during the past years (p-value < 0.05, Sens's slope = − 0.002). The Mella River is the only one among the investigated water courses to show an increase in $NO_3^-$ concentration through time both upstream (p-value < 0.05, Sens's slope = 0.015) and downstream (p-value < 0.05, Sens's slope = 0.04) the groundwater input. The full output of trend analysis of rivers N forms is reported in the Supplementary Material (Table A4).

Given the strong interaction between groundwater and rivers in the investigated area, a transfer of N from contaminated groundwater to surface water is expected. To test this hypothesis, data from the specific samplings in 2022 and 2023 were used, since the sampling stations were selected expressly to characterize the river-groundwater interaction.

Differences in $NH_4^+$ and $NO_2^-$ concentrations were not statistically different between the inside and outside of the river-groundwater interaction area in the three rivers. In the Mincio River, inside and outside of the river-groundwater interaction area average concentrations were 88 μg $NH_4^+$ $L^{-1}$ ($F(1) = 0.41$, $p > 0.05$) and 70 μg $NO_2^-$ $L^{-1}$ ($F(1) = 0.08$, $p > 0.05$). In the Chiese River, average concentrations were 71 μg $NH_4^+$ $L^{-1}$ ($F(1) = 1.4$, $p > 0.05$) and 129 μg $NO_2^-$ $L^{-1}$ ($F(1) = 2.02$, $p > 0.05$). Finally, in the Mella River, average concentrations were 394.5 μg $NH_4^+$ $L^{-1}$ ($F(1) = 0.77$, $p > 0.05$) and 182 μg $NO_2^-$ $L^{-1}$ ($F(1) = 3.38$, $p > 0.05$). Only $NO_3^-$ concentrations increased inside the river-groundwater interaction area. The Mincio River shows a 2-fold increase of $NO_3^-$ downstream the river-groundwater interaction area (Fig. 7). The linear mixed effect model confirmed that this difference is statistically significant ($F(1) = 11.645$, $p < 0.001$) and the groundwater input increased $NO_3^-$ concentration from 4.78 mg $NO_3^-$ $L^{-1}$ to 11.65 mg $NO_3^-$ $L^{-1}$ on average. Downstream the groundwater input, the rise in $NO_3^-$ concentration was not associated with the irrigation period, from April-September ($F(1) = 1.15$, $p > 0.05$). The groundwater input is even more marked in the Chiese and Mella rivers, where the $NO_3^-$ concentration is higher downstream the groundwater interaction stretch regardless the sampling period (Fig. 7).

In the Chiese River, the linear mixed effect model highlighted a highly significant increase in $NO_3^-$ concentration downstream the groundwater input ($F(1) = 18.36$, $p < 0.001$), from 5.31 to 12.53 mg $NO_3^-$ $L^{-1}$ on average. Downstream the groundwater input, the increase in $NO_3^-$ concentration (from 9.61 to 12.45 mg $NO_3^-$ $L^{-1}$ on average) depended on the irrigation period (April-September) ($F(1) = 8.94$, $p < 0.01$). Also in the Mella River, results from the linear mixed effect model suggest a highly significant difference in $NO_3^-$ concentration downstream the groundwater input ($F(1) = 8.88$, $p < 0.001$), increasing from 11. 28 to 29.03 mg $NO_3^-$ $L^{-1}$ on average. Downstream the groundwater input, the increase in $NO_3^-$ concentration did not depend on the irrigation period ($F(1) = 1.67$, $p > 0.05$).

### 3.4. Identifying contamination sources: Insights from the SSB of nitrogen

SSB calculations showed a diffuse N surplus across all three watersheds during the investigated period (Fig. 8), with manure from animal farming representing the main N input to arable land (60 %) for all the three watersheds during the investigated period. The highest surplus is observed in the Chiese watershed, peaking at 185 kg N/ha $y^{-1}$ in 2010, and still displaying the higher surplus (141 kg N/ha $y^{-1}$) among the three watersheds according to the latest available data (2020). All three watersheds showed a decrease in the surplus from 2000 to 2020, mainly due to a marked decrease in synthetic fertilizers use (42 %-61 %) for all the three watersheds, and a slight decrease in manure application (20 %), only for Mella and Mincio in the last two decades. In fact, the greatest reduction was observed in the Mella watershed, where the surplus in the recent years is almost 40 % of the surplus in 2000.

### 3.5. Application of the LIMeco index for ecosystem health assessment

The trophic status of the three rivers in their alpine portion fell within the "High" or "Good" classes (Table A5). Moving downstream the LIMeco index shifts to lower classes, with a different trend for each river. The Mincio River has a good trophic status from its origin up to station MN4. Between stations MN4 and MN6, it shifts from "High" to "Sufficient". Although a slight increase in the LIMeco value is achieved in the downstream stations, the trophic status never recovers to its original value. The worst trophic level was measured in 2018, when the sampling station ME6 had concentrations of 11.6 mg $NO_3^-$ $L^{-1}$, 91 μg $NH_4^+$ $L^{-1}$, and an $O_2$ saturation of 79 % on average, leading to a final LIMeco score of 0.16 (class "Bad"). The trophic status of the Chiese River is classified as "High" from its origin to station CH4 and, from here, it progressively decreases to the class "Sufficient". In 2016, it reached the worst

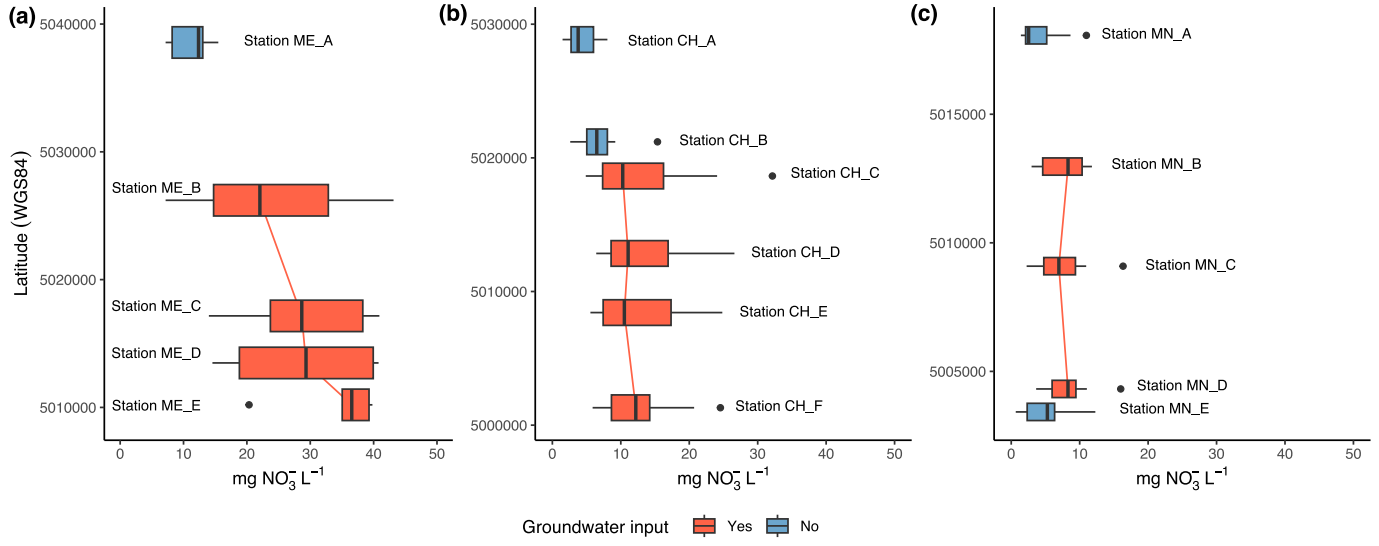


**Fig. 7.** $NO_3^-$ concentration in the three rivers during 2022–2023. The station names from Fig. 1 are reported beside every boxplot, colored according to its position compared with the river-groundwater interaction area. The station MN_E has been considered as "upstream" because it is located within the Mantua upper lakes, which hinder the effect of groundwater.

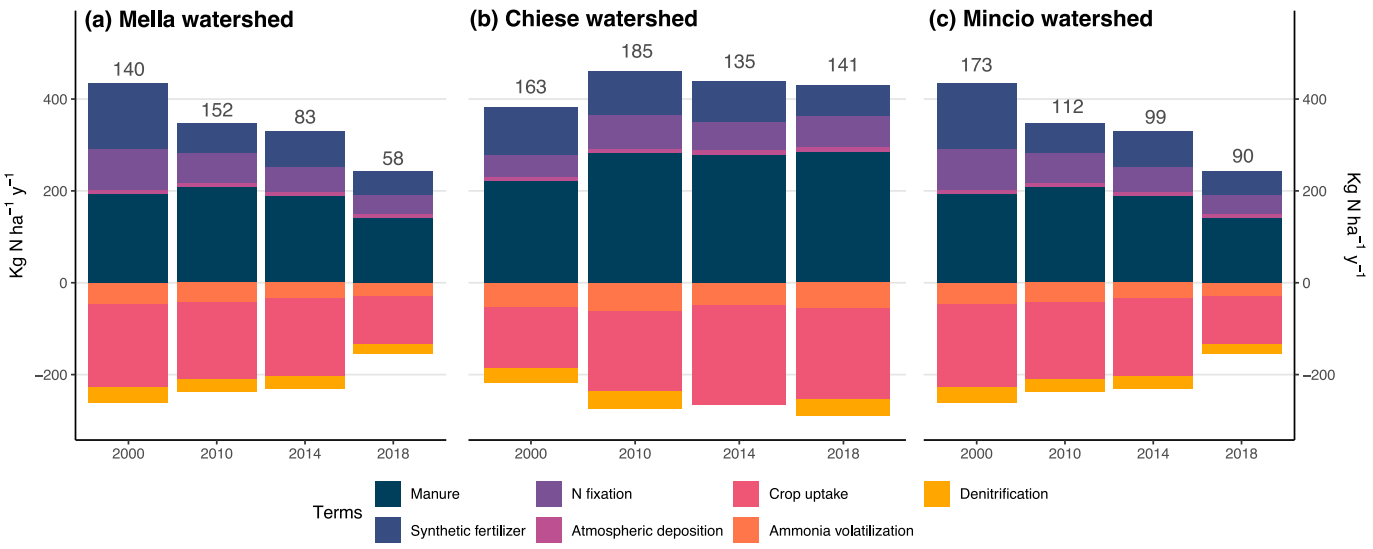


**Fig. 8.** SSB of the three watersheds, the dark colors represent the inputs, the lighter ones the outputs. Above every bar, the final result of the SSB, i.e. the surplus, is reported.

condition, being classified as "Bad", with 14.2 mg $NO_3^-$ $L^{-1}$, 160 μg $NH_4^+$ $L^{-1}$, and 90 μg P/L on average. Contrary to the Mincio River, there is no improvement of the LIMeco value in the last section of the river. Finally, the Mella River shows the worst trophic status of all. The LIMeco class is "High" up to station ME3, except for 2020 when the trophic status was classified as "Sufficient" also in the alpine portion. From station ME3, the trophic status decreases to "Sufficient" and "Poor", without successive improvements. The worst trophic status has been measured in 2016, with 24.4 mg $NO_3^-$ $L^{-1}$, 319 μg $NH_4^+$ $L^{-1}$, and 237 μg P/L on average. The N:P molar ratio increases significantly downstream the groundwater inputs in the Mella River ($F(1) = 7.40$, $p < 0.01$) and in the Chiese River ($F(1) = 8.43$, $p < 0.01$), but not in the Mincio River ($F(1) = 0.73$, $p > 0.05$).

## 4. Discussion

### 4.1. Dynamics within the soil-groundwater-river nexus

Analyzing the hydrochemical features of the aquifer enable the identification of key geochemical facies and the detection of mixing occurrences among waters originating from distinct recharge zones (Freeze and Cherry, 1979; Hem, 1985). Groundwater in the three watersheds had very similar chemistry, proving the spatial continuity of the alluvial aquifer investigated and the (bio)geochemical processes within it (Fig. 4). This uniformity is suggested also by the concentration of N forms (see Section 3.3). Ionic ratios indicate an excess of $Ca_2^+$ and $Mg_2^+$ that likely originates from reverse ion exchange reactions (Datta and Tyagi, 1996). When $HCO_3^-$ and $Ca_2^+$ in groundwater are solely derived from calcite dissolution, their equivalent ratio should be approximately 1:2. In contrast, if they originate from dolomite dissolution, the ratio should be around 1:4 (Holland, 1978; Mackenzie and Garrels, 1971), indicating that carbonate dissolution plays a significant role in determining the final water chemistry. Only $HCO_3^-$ changed along the groundwater flowpath from N to S. Such increase can be ascribed to the dissolution of carbonate deposits, which comprise the primary minerals found in the aquifer (Bruno et al., 2017). N biogeochemical cycling can also influence $HCO_3^-$ concentration. The organic N mineralization and nitrification can act as main sources of protons, leading to carbonate dissolution (Guy et al., 2013; Perrin et al., 2008). In the context of strong organic N fertilization, as described in the study areas, these processes could be responsible for a significant increase in $HCO_3^-$ concentrations. The observed uniformity in groundwater chemistry across the watersheds provides valuable insight into regional biogeochemical processes. This uniformity suggests a well-integrated aquifer system, influencing not only local but potentially regional water quality management strategies (see Section 4.3).

The interaction between river and groundwater in specific sectors of the study area has been already characterized. The Mincio River, previously investigated only in the portion between the sampling stations MN4 and MN_B, is configured as a flow-through system, gaining groundwater from its right bank and recharging groundwater in its left bank (Severini et al., 2022). This configuration brings a change in river chemistry without major changes to its discharge. From stations MN_B to MN_6, water table from Fig. 1b highlights a gaining river section, with a change in river discharge as well. On the contrary, the Chiese River gains groundwater from the aquifer from the central part of its course to its end, with higher inputs outside the irrigation period (summer) due to the lowering of groundwater level (Fig. A1) promoted by irrigation (Severini et al., 2023). The Mella River has received little attention from the scientific community, although several studies were performed within the Oglio watershed, which includes it. Here, the groundwater level increases by several meters at the end of the irrigation period due to the aquifer recharge from irrigation practices. Additionally, a gaining condition of the rivers has been hypothesized due to groundwater-river interactions based on hydrochemical and isotopic data of the southern portion of their course (Rotiroti et al., 2019; Taviani et al., 2020).

The large use of water (for flood irrigation), the vast network of irrigation channels, and the diffuse river-groundwater interaction highlight how the soil-groundwater-river nexus is a key aspect as driver of eutrophication in the investigated catchments. Our findings align with previous studies on groundwater and river quality in similar agro-ecological settings, but differ in the extent of $NO_3^-$ impact observed, which could be attributed to regional differences in irrigation practices (Spruill and Bratton, 2008; Yoshikawa et al., 2015; Yu et al., 2018). As such, different factors must be considered to comprehend the pollution dynamics of both surface and groundwater. Following the path of a water drop over the fields, the first issue is given by the N stored in the soil. Soil System Budget revealed a large N surplus in the three watersheds. Although N surpluses decreased in the past 20 years, their values are still dangerously high, with 58 kg N/ha $y^{-1}$, 141 kg N/ha $y^{-1}$, and 90 kg N/ha $y^{-1}$ for the Mella, Chiese, and Mincio watersheds, respectively. Batool et al. (2022) performed a long-term evaluation of annual soil N surplus across Europe for the period 1850–2019, finding that the highest N surplus is ~ 140 kg N/ha $y^{-1}$. This value is comparable to those

calculated for the Chiese and Mincio watersheds, pointing out how the Po Plain is a relevant hotspot of N excess at the European level.

The overabundant accumulation of N in soil does not constitute a reservoir for future crops. This a consequence of the main irrigation in these catchments, i.e. flood irrigation (Pinardi et al., 2022; Racchetti et al., 2019; Rotiroti et al., 2019; Severini et al., 2023; Soana et al., 2011). This technique, besides providing large amounts of water to crops, promotes the aquifer recharge and favors the percolation of N stored in soil and the underlying vadose zone to the saturated zone. The availability of N from applied manure, which is the main N input, encompasses both the organic N and inorganic N components ($NO_3^-$ and $NH_4^+$) produced via mineralization (Eghball, 2000; Eghball et al., 2002). Eventually, N in groundwater is mostly $NO_3^-$ in the hill portion and high plain, where there is interaction between groundwater and surface waters. The high $O_2$ concentration in this portion of the aquifer (Table A2) also hinders denitrification, at least in the shallow portion of the saturated zone. In the deeper portion, sub-oxic and anoxic niches could be found, since the investigated wells have usually high $N_2$ excess, supporting the occurrence of denitrification (Severini, unpublished data). The irrigation technique itself could be central in keeping the oxidizing redox conditions, due to the continuum percolation of water with high $O_2$ concentration (Severini et al., 2023). The percolated $NO_3^-$ accumulates in groundwater and, where groundwater feeds rivers, a steep increase in $NO_3^-$ in surface waters is generally found, affecting rivers' trophic status and ecological functioning.

The increase in $NO_3^-$ concentration in rivers is regulated by three factors: i) $NO_3^-$ concentration in groundwater, ii) the river flow upstream the interaction area, and iii) hydraulic gradient between surface waters and groundwater. All the investigated N forms showed almost constant trends in groundwater during the investigated period. Only $NH_4^+$ concentration decreased in the hill portion and high plain, probably due to the decrease in manure application (20 %) for the Mella and Mincio catchments as evidenced by the SSB. The other forms remained stable, also due to the constant and overabundant N input to the soil, leading to the diffuse N legacy sources. The second factor shaping the increase in $NO_3^-$ concentration in rivers is the discharge of the river itself, which can effectively dilute the contaminated groundwater input. The Mincio and Chiese rivers originate from two alpine lakes that act as water reservoirs during the non-irrigation period (October-April), and release larger flows for irrigation purposes during spring and summer. During summer, the discharge is higher in the Mincio River because local authorities (e.g. irrigation and land reclamation consortia) must provide enough water for flood irrigation and respect a minimum vital flow of the river (MVF, $\sim 7\ m^3\ s^{-1}$). In the Chiese River, the same principle is applied, but Lake Idro is a small reservoir, and it can happen that water released from the lake is completely diverted to irrigation channels, not respecting the river's MVF of $\sim 5\ m^3\ s^{-1}$ and drying out the river, as happened during summer 2022 at the sampling station CH_B (Fig. A5) (Severini et al., 2023). The Mella River does not originate from a lake and, during summer, the riverbed is dried out for irrigation purposes, usually between the sampling stations ME5 and ME_C. Pictures of the three rivers in critical sections during the irrigation period are reported in Fig. A5. Finally, the increase in $NO_3^-$ concentration in rivers is regulated by the hydraulic gradient between rivers and groundwater. The highest the hydraulic gradient is, the highest is the volumetric input of groundwater to the rivers. In this area, groundwater heads can fluctuate up to three meters between the irrigation and non-irrigation periods. In the Mincio watershed, the aquifer recharge given by flood irrigation has the potential to rise by up to $\sim$ 3 m groundwater heads, fostering the groundwater input to the river. Outside the irrigation period, the groundwater input is lower (Pinardi et al., 2022; Severini et al., 2022). A similar trend has been reported in the Oglio watershed, which includes the Mella River, with rises of groundwater heads up to $\sim$ 4 m (Rotiroti et al., 2019). On the contrary, in the Chiese watershed, the water table is lower during the irrigation period and the volumetric input to surface water is lower as well (Fig. A1). This is due to the use of groundwater for irrigation, which is lost due to evapotranspiration lowering the water table (Severini et al., 2023). This hydrogeological functioning agrees with the groundwater inputs measured during 2022–2023 in our study area (Fig. 3), with higher groundwater inputs during summer in the Mincio and Mella rivers and an opposite trend in the Chiese River, with higher values outside the irrigation period.

Due to the strong effect of aquifer recharge and N transport given by irrigation, positive feedback of irrigation on $NO_3^-$ concentration in the rivers was expected, but it was significant only in the Chiese River due to the mechanism postulated in Severini et al. (2023). In this watershed, irrigation practices promote the percolation of applied N fertilizers, hinder $NO_3^-$ denitrification due to dominant oxic conditions of groundwater and dry the Chiese River. River sectors downstream dried sections are exclusively fed by $NO_3^-$ contaminated groundwater inputs. The significant increase in $NO_3^-$ concentrations due to flood irrigation suggests a need for revising nutrient cycling models to incorporate the effects of flood irrigation more accurately, as recently explored by Hou et al. (2024), Pool et al. (2022), and Zhang et al. (2021). In the Mincio River, an increase in $NO_3^-$ concentration during the irrigation period has been registered, but it was not significant. This is likely due to the dilution of $NO_3^-$ inputs from groundwater and the high discharge of the river during this period. Lakes can work as upstream buffers, lowering nutrients concentration thanks to the metabolism of primary producers and denitrifying microbial community (Mats et al., 1994; Saunders and Kalff, 2001). Lakes also work as water reservoirs, accumulating water during intense precipitation periods and releasing water during irrigation or dry periods. The Mella river does not originate from a lake and lack these potential buffer mechanisms. As a consequence, the surface N inputs during winter and spring precipitations are similar to $NO_3^-$ input during the irrigation period given by groundwater, resulting in similar $NO_3^-$ concentration in the river during the year. This is unexpected for this watershed since a strong effect of irrigation period is usually observed in this area (Pinardi et al., 2022; Racchetti et al., 2019; Severini et al., 2022; Taherisoudejani et al., 2018), but it is not for other watersheds, where higher nutrients exports are measured during winter and spring precipitation (e.g. de Klein and Koelmans, 2011; Kincaid et al., 2020; Vink et al., 2007; Vybernaite-Lubiene et al., 2018).

In the final analysis, the investigated area is characterized by a close circulation of water among soil, groundwater, and rivers. The diffuse N surplus provides a continuous source of contamination, which is driven to groundwater thanks to flood irrigation. Groundwater has been contaminated for the past decade, mainly with $NO_3^-$ in the hill and high plain portions of the aquifer. Moving from the high plain to the low plain, a strong interaction between (gaining) rivers and groundwater has been measured, under both volumetric and chemical perspectives. The consequence of this situation is a diffuse $NO_3^-$ input into rivers, which severely alters their trophic status.

### 4.2. Groundwater contributions to eutrophication: Assessing the impact

The LIMeco index classification proves to be highly stringent, especially concerning $NO_3^-$ and P parameters (Azzellino et al., 2015). Nevertheless, recent studies suggest that, in the Po Plain, the thresholds for $NO_3^-$ and total P set by the Italian legislation for water quality classification should be far more stringent to reflect a truly "Good" ecological status (Bona et al., 2024). In all three investigated rivers, the LIMeco index highlighted a "Good" ecological status in the alpine portion, due to the lower anthropogenic pressures compared to the plain area (Fig. 9). In the alpine portion, agriculture and livestock production are indeed more extensive, with lower N inputs from fertilizers, and there are no large urban areas and no large WWTPs consequently.

From there, the ecological quality decreases, highlighting an elevated trophic status. This worsening of trophic conditions is common for all three watersheds and is (mostly) located within the river-groundwater interaction area (Fig. 9). Here, the increase in $NO_3^-$ concentration along the river's courses given by groundwater inputs has a

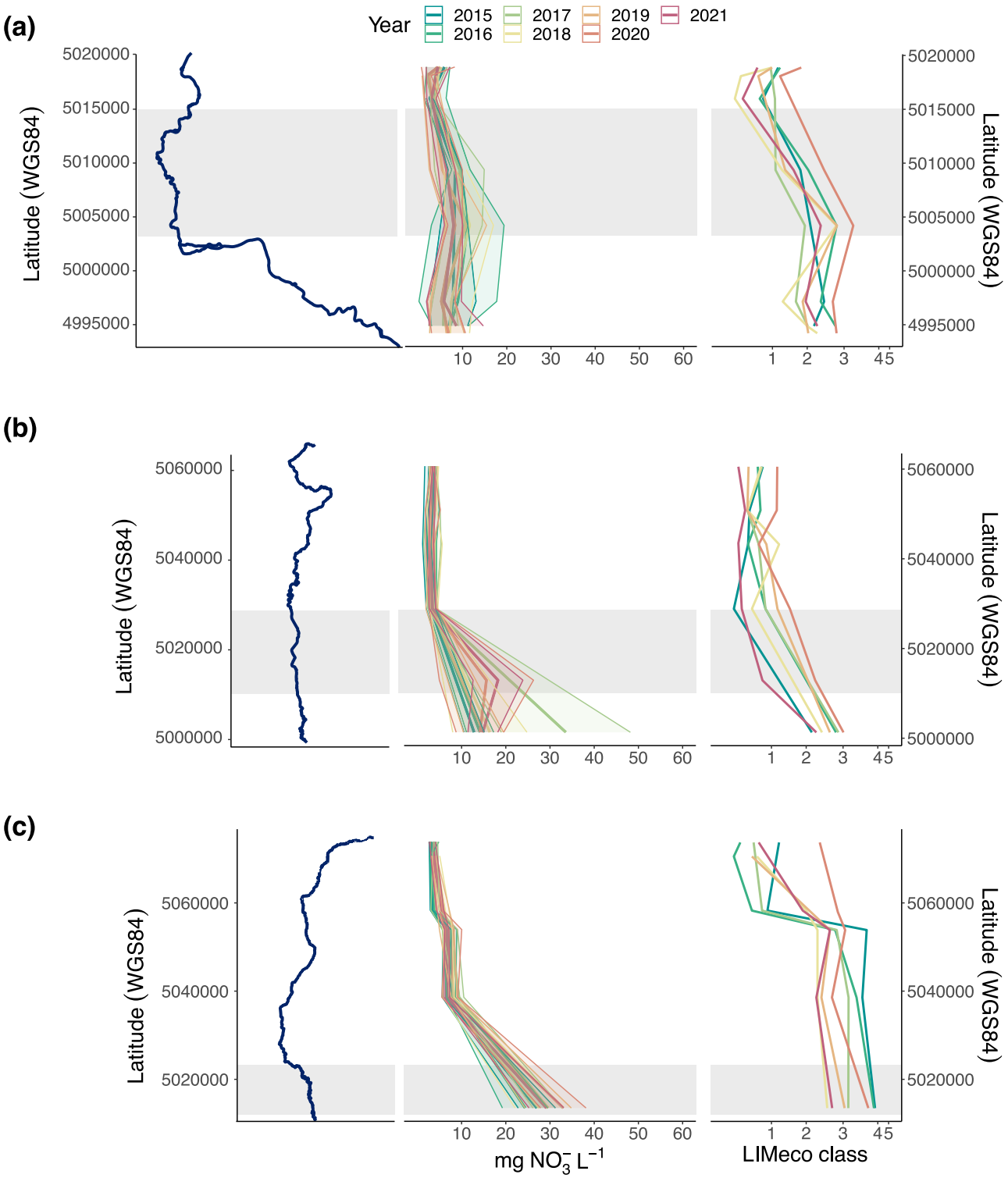


**Fig. 9.** From left to right in each panel: part of the river course including the river-groundwater interaction sector (in grey), $NO_3^-$ concentration, and the LIMeco index in the Mincio (a), Chiese (b), and Mella (c) rivers.

trend comparable to that of the LIMeco index, proving its central role in modifying the trophic level (Fig. 9). In groundwater, N concentrations are much higher than those measured in rivers. Nevertheless, they still have severe effects on the ecological quality of the riverine ecosystems, which can be affected by even small changes in nutrients concentrations and molar ratios. The LIMeco index accounts also for $O_2$, $NH_4^+$, and total P concentrations, which have heterogeneous effects on the trophic level. Groundwater input lowers $O_2$ concentration in rivers, but the decrease is minimal, it does not affect the river ecosystem and the LIMeco index for this parameter remains usually within classes "Good" or "High". $NH_4^+$ input from groundwater is unimportant since it is almost absent due to the oxidizing condition of the aquifer in the hill and high plain portion.

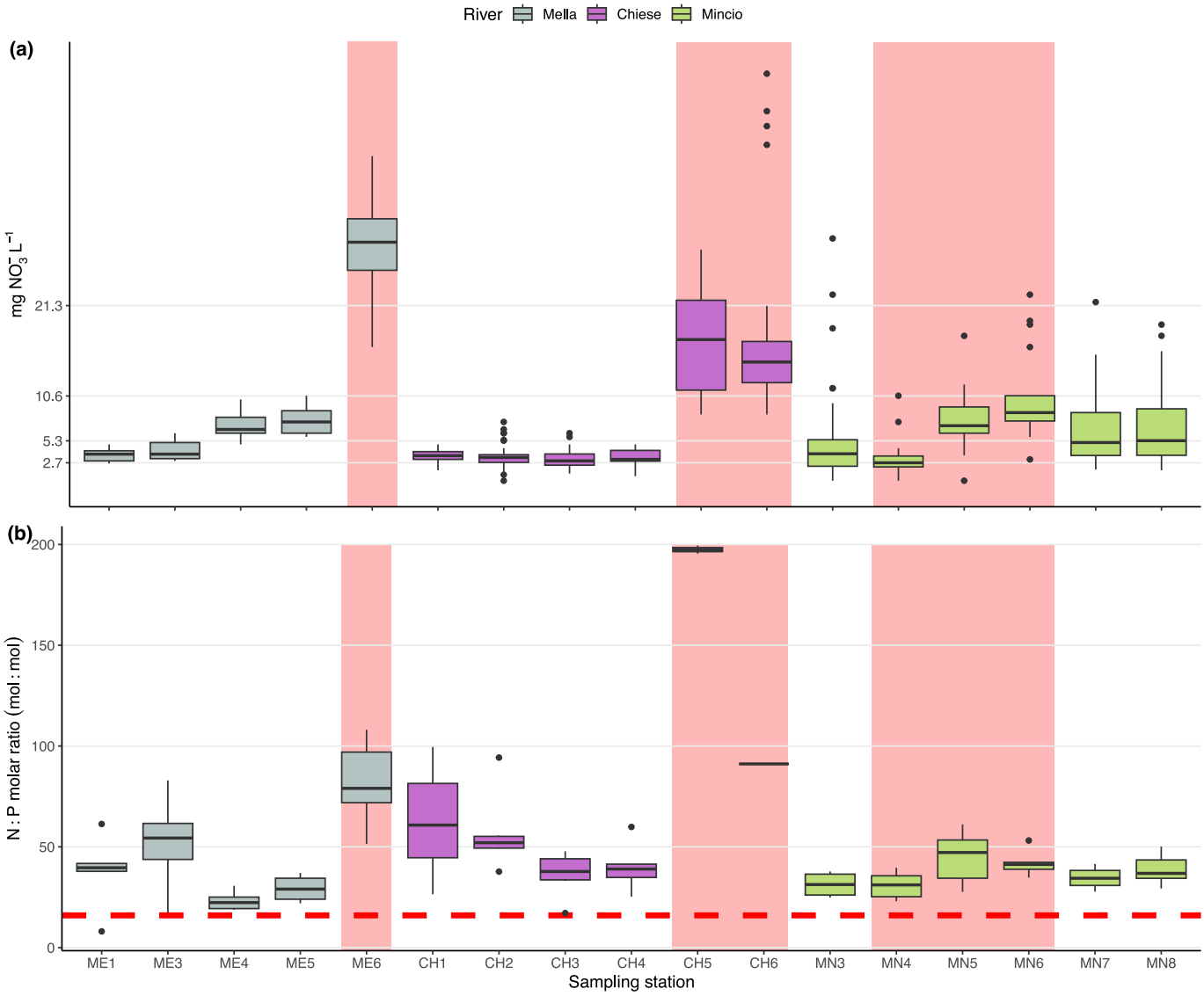


**Fig. 10.** (a) $NO_3^-$ and (b) N:P molar ratio along the three rivers in the period 2015–2021. The continuous lines in (a) set the limits for the LIMeco classes. The dashed red line in (b) indicates the theoretical Redfield ratio (N:P = 16:1). The red areas indicate the stations within the river-groundwater interaction area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Its presence in rivers can be associated with point sources like WWTPs. They are diffused along the river course, but their N and P input is usually diluted or consumed within a few km. The Mella River constitutes an exception to this scenario. Here, The LIMeco index rapidly decreases to the "Sufficient" and "Poor" classes at station ME4, well above the river-groundwater interaction area. The worsening of trophic status is caused by the input of untreated sewers collecting wastewater from all the alpine portion of the watershed, with almost 50,000 inhabitant equivalents (IE). This discharge severely increases $NH_4^+$ and total P concentration in the Mella River, worsening the trophic status. A new WWTPs was activated in 2020 and, according to our data, the LIMeco index slightly improved. Between sampling stations ME5 and ME6, river-groundwater interaction contributes to further increasing the trophic status of the river and the LIMeco index drops to the class "Poor". Here, the worst trophic status was calculated in 2016, where the station ME6 had concentrations of 24.4 mg $NO_3^-$ $L^{-1}$, 280 µg $NH_4^+$ $L^{-1}$, and 237 µg P/L, with a LIMeco score of 0.04 (class "Bad"). Lastly, total P has a variable LIMeco value, falling from the classes "Good" to "Poor". Its presence in surface waters is usually low in these rivers, where the annual load is transported mainly during flash floods (Viaroli et al., 2018), but can increase after inputs from WWTPs. This factor has an undeniable effect on the LIMeco value but is not as pivotal as $NO_3^-$. The average concentrations of total P and $NH_4^+$ vary between the "High" and "Good" classes and, only in the Mella River, $NH_4^+$ varies between the "Good" and "Bad" classes (Fig. A6). On the contrary, $NO_3^-$ input has far harsh consequences, lowering the trophic class from "Good" to "Sufficient" (Mincio River), from "Good" to "Sufficient" (Chiese River), and from "Sufficient" to "Bad" (Mella River) (Fig. 10a).

The N:P molar ratio suggests a generalized N excess, with peaks in the river-groundwater interaction area, in particular in the Chiese and Mella rivers. In the Mincio River, the increase of N:P ratio was not so pronounced, probably due to the presence of P sources like small WWTPs. In the Mella and Chiese rivers, the N:P ratio deviated many-fold from the theoretical Redfield Ratio (N:P = 16:1, Fig. 10b), suggesting an excess of N relative to P, which is a limiting nutrient. This stoichiometry shift may produce large changes in species composition in the primary producer communities, further fostering eutrophication and hindering future actions to restore the original structure and species composition

in river and marine ecosystems (Duarte et al., 2009; Glibert, 2017). These N:P ratios are very close to those calculated by Viaroli et al. (2018) in the whole Po River watershed, pointing out that the diffuse N input from groundwater is a widespread issue of the Po Plain.

Based on the evidence presented, it is clear how $NO_3^-$ is the main factor affecting eutrophication in the investigated rivers and it is mostly derived from diffuse groundwater inputs. In the investigated watersheds, wastewaters also showed an effect on eutrophication in terms of LIMeco value due to their $NH_4^+$ and P inputs. Nevertheless, it is easier to contrast point sources rather than diffuse ones, and few interventions could have significant benefits on river $NH_4^+$ and P inputs, as happened with the construction of the WWTP upstream sampling station ME4 in the Mella River. Groundwater constantly delivers $NO_3^-$ to the rivers, and their elevated $NO_3^-$ concentrations can only be contrasted by a higher river flow, which promotes dilution. This is a short-time solution, able only to decrease the LIMeco final value, but the trophic status could not improve at the same rate, since $NO_3^-$ loads (concentration × discharge) would remain high.

## 5. Concluding remarks

River-groundwater interaction in the Po Plain has always played a significant role and it has not been always negative. In the whole plain, moving from the high to the low plain, the presence of abundant lowland springs historically allowed the plain to be a productive agricultural area. These springs were used for irrigation and water meadows and today, in a more urbanized context, they are considered hotspots of biodiversity and important wildlife corridors (Bischetti et al., 2012; Fumagalli et al., 2017). The general increase in river discharge given by groundwater inputs allowed the use of larger volumes of water for flood irrigation, a practice still relevant today, as described in Sections 1.1 and 4.1.

River-groundwater interaction, as well as the numerous springs, in the past had positive feedback on the ecosystem and was not associated with eutrophication. Starting from the late 20th century, the water chemistry of groundwater and of springs, consequently, has changed due to an excess use of fertilizers (both synthetic and organic) in the Po Plain, which is still today a primary issue, with N inputs among the highest measured in Europe (De Vries et al., 2021). In this context, the close connection between flood irrigation and river-groundwater interaction does not promote the recycling of water and the connected ecological services but constitutes the main mechanism of N loss, transport, and contamination. Reducing the N surplus is prospected as the only solution to contrast eutrophication in these agricultural watersheds. European directives like the Nitrate Directive (91/676/EEC) and the new EU's common agricultural policy (CAP) for the period 2023–2027 are working in this direction. To reduce the N surplus, possible solutions include facilitating denitrification in cultivated fields (Soana et al., 2023; Wang et al., 2018), and switch from manure to slow-releasing N-fertilizers (Timilsena et al., 2015) to contrast leaching, volatilization, and nitrification.

Moreover, scenario simulations performed in the Po River lowlands highlighted that promoting denitrification in the canal networks by implementing vegetation-preserving management practices may be an effective tool to contribute to achieving a WFD good ecological status (Soana et al., 2023).

Leaching and runoff are also responsible for dislocating N surplus from soil to water. A more efficient irrigation management could be also considered at watershed scale, like switching from flood irrigation to more water-efficient irrigation (e.g. drip irrigation, García-Garizábal et al., 2012). Extreme hydrologic events, i.e. intense rainfall events, can also promote N and P runoff from agricultural fields (Kleinman et al., 2006) and fertilization timing could be scheduled far from periods of such extreme conditions, such as spring and autumn in the Po Plain, where these correlations were already reported (Viaroli et al., 2018). To successfully reduce N surplus, many side factors must be accounted for, like lag times, suboptimal placement and distribution of BMPs within the watershed, post-implementation BMP malfunctions, socio-political and economic obstacles, and farmer perspectives on irrigation efficiency (Knox et al., 2012; Lintern et al., 2020). River restoration projects across Europe using BMPs have consistently proven their effectiveness, highlighting their key role in revitalizing riverine ecosystems. However, these projects also show that merely applying existing regulations is insufficient for restoring contaminated ecosystems (Castaldelli et al., 2015; Chittoor Viswanathan and Schirmer, 2015; Morandi et al., 2014; Ricci et al., 2022; Soana et al., 2019). In the context of reduced N surplus, the springs and groundwater inputs to rivers could gain their original role and further promote the dilution of point sources of contamination. According to the results provided in this work, the improvement of the trophic status in these watersheds will require time, especially to deal with the N legacy, but a few preliminary and promising results were already obtained (Severini et al., 2022).

From a broader perspective, the peculiarity of the investigated region allowed us to follow the dynamics of the soil-groundwater-river nexus which could soon become central for irrigated areas at a global scale. The region has been historically favored by large water availability from Alpine Lakes. Only recently the irrigation source started shifting from surface waters to shallow wells, and groundwater is becoming central for irrigation (Severini et al., 2023) with consequences on both groundwater and rivers quality. This shift in irrigation supply will lead to a lowering of the water table and a higher nitrifying potential of soil and vadose zone, increasing the threat of $NO_3^-$ contamination (Ascott et al., 2017; Siebert et al., 2010), make the N oxidizing processes more important than reductive ones (Clague et al., 2019). On global scale, there has been a significant surge in the use of irrigation water to enhance food production, witnessing an increase from ~650 in 1960 to ~1400 $km^3\ yr^{-1}$ in 2010 (Wada and Bierkens, 2014). This trend was supported by over-abstraction of surface waters and groundwater, which increased by almost 50 % (Wada and Bierkens, 2014). As seen in the investigated watersheds, the unpairing between agriculture practices, e.g. fertilization, and water management leads to a significant $NO_3^-$ contamination of groundwater and, due to river-groundwater interaction, severe eutrophication problems in the related rivers. This work also underscores the intricate relationship between surface and groundwater in agricultural watersheds, requiring water management with broad environmental awareness. It emphasizes the need for coordinated hydrogeological and ecological approaches, which is central to the emerging field of "Ecohydrogeology". This discipline explores the interactions between ecology and hydrogeology, focusing on feedback loops between surface ecosystems and groundwater, as demonstrated in this manuscript.

## CRediT authorship contribution statement

**Edoardo Severini:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Monia Magri:** Writing – review & editing, Writing – original draft, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Elisa Soana:** Writing – review & editing, Validation, Formal analysis, Data curation. **Marco Bartoli:** Writing – review & editing, Writing – original draft, Project administration, Investigation, Conceptualization.

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## 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.

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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.2024.132185.

## Data availability

Data will be made available on request.

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