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Research papers

Groundwater and surface water nitrate pollution in an intensively irrigated system: Sources, dynamics and adaptation to climate change

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ABSTRACT

Freshwater pollution by nitrate is a major threat to human and ecosystem health. Basin-scale studies on nitrate pollution generally focus separately on surface water or on groundwater bodies, thus the role played by their interaction on nitrate concentrations, possibly including also agricultural irrigation, is often overlooked and so is addressed here in the intensively irrigated hydro-system of the Oglio River basin (Northern Italy). Tracers of groundwater recharge (stable water isotopes and Cl/Br ratio) together with nitrate and boron stable isotopes indicate that the main source of the diffuse nitrate pollution affecting groundwater resources in the area is related to agricultural activities and, locally, to untreated civil/industrial effluents. Moreover, these data reveal the strong control of irrigation return flow on groundwater nitrate concentrations, with contrasting effects: groundwater-fed irrigation promotes higher concentrations due to the recirculation of high-NO_3 groundwater, whereas intensive surface-water-irrigation, fed by low-NO_3 river water, generates lower concentrations due to dilution. The control of irrigation return flow on groundwater nitrate links nitrate pollution and climate change: if surface-water-irrigation will be abandoned, as a consequence of intensified summer droughts, in favor of groundwater-fed irrigation, an increase in groundwater nitrates is expected due to a basin-scale groundwater recirculation and the cessation of the dilution effect. In addition to the reduction of the N input to soils from fertilizers, i.e., the sole pollution mitigation strategy able to solve the problem, an adaptation strategy to climate change might be the implementation, during non-irrigation rainy periods, of managed aquifer recharge operations, such as the so-called “forested infiltration areas”, to take advantage of water abundancy from rivers under high-flow conditions, thus combining a supplement on groundwater recharge with the beneficial dilution effect on dissolved nitrate.

1. Introduction

Water pollution by nitrate stands as a major global threat to the health of humans and ecosystems (Bijay-Singh and Craswell, 2021; Burri et al., 2019; Gomez Isaza et al., 2020; Ward et al., 2018). Concerning human health, high nitrate in drinking water may lead to an increased risk of colorectal cancer, thyroid disease and neural tube defects, in addition to infant methemoglobinemia (blue baby syndrome; Ward et al., 2018). It follows that the use of low-nitrate water for human consumption is key for protecting public’s health.

Commonly, freshwater nitrate pollution at basin scale is investigated by studies that focus separately on surface water or on groundwater bodies (e.g., Abascal et al., 2022; Liu et al., 2020; Nestler et al., 2011; Zhang et al., 2021). However, interactions between surface waters and groundwaters are of fundamental importance in hydro-system dynamics, influencing reciprocally surface water and groundwater qualities. Therefore, a holistic approach jointly investigating surface water and groundwater bodies is recommended in basin-scale studies tackling nitrate pollution (e.g., Lasagna et al., 2016; Li et al., 2014; Mellander et al., 2014; Zhang et al., 2014). Moreover, in many agricultural watersheds, irrigation has altered the natural hydrodynamics, becoming an important anthropogenic component that affects the whole hydrological system (Wagener et al., 2010), being, for instance, a fundamental source of groundwater recharge as irrigation return flow (Séraphin et al., 2016;

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Taylor et al., 2013). It follows that, in intensively irrigated systems, studies aiming at assessing the sources and processes that determine water nitrate pollution cannot disregard the interactions among surface water, irrigation water and groundwater. Irrigation return flow has frequently a negative impact on groundwater quality, promoting the leaching of fertilizers from agricultural soils to aquifers, so generating high-NO_3 groundwaters (Chen et al., 2010; Diez et al., 2000; Poch-Massegú et al., 2014; Schmidt and Sherman, 1987; Yesilnacar and Gulluoglu, 2008). However, where large volumes of irrigation water having low NO_3 concentrations are used, return flow can have beneficial effects on groundwater quality due to dilution (Böhlke et al., 2007; Bouimouass et al., 2022; Castaldo et al., 2021; Rotiroti et al., 2019a).

A good example of hydro-system altered by irrigation and strongly affected by nitrate pollution is the Po Plain of Northern Italy (Martinelli et al., 2018; Viaroli et al., 2018). The Po Plain hosts one of the largest aquifer systems in Europe (Van der Gun, 2022) that is featured by a strong interaction with surface and irrigation waters (Giuliano, 1995). Moreover, in recent years, the Po Plain area has been increasingly impacted by extreme events due to climate change (heat waves, droughts and floods), aggravating the conflicts among stakeholders due to multiple water uses (Musacchio et al., 2021, 2020). The Oglio River basin, a sub-basin of the Po River, is an interesting case study since it is subjected to intense irrigation and is affected by a strong nitrate pollution of both surface water and groundwater. Previous studies in this area revealed how nitrates are transferred from groundwater to surface water bodies (Bartoli et al., 2012; Delconte et al., 2014; Rotiroti et al., 2019a), but some knowledge gaps still need to be filled to obtain a comprehensive understanding of the hydro-system functioning. The works by Bartoli et al. (2012) and by Delconte et al. (2014) were based on a few groundwater samples, and nitrate pollution dynamics in groundwater could not be properly pinpointed. The work by Rotiroti et al. (2019a) identified a hotspot of groundwater nitrate pollution in the piedmont area, but the limited data available for this area prevented an in-depth investigation of the nitrate hotspot cause.

The main aims of the present work are to (1) assess the origin of water nitrate pollution, (2) identify the main processes controlling nitrate dynamics and (3) suggest some pollution mitigation and climate change adaptation strategies to reduce the impact of nitrates in a hydro-system featured by strong surface-water/irrigation-water/groundwater interactions: the Oglio River basin. The intent of this work is to provide indications to support a sustainable water management by local authorities to mitigate the increasing anthropogenic and climate change impacts. Moreover, as a typical example of a hydro-system with complex surface-water/irrigation-water/groundwater interactions, the identification of the key processes regulating nitrate pollution will be useful in other areas with similar features worldwide. To fill the previously mentioned knowledge gaps, this work is based on an extended groundwater dataset also covering the nitrate hotspot of the piedmont area. The objectives of this study are achieved by using (1) a relatively dense monitoring network to draw a representative picture of water nitrate pollution in the area, (2) end-member mixing models using conservative tracers of groundwater recharge, such as stable water isotopes (δ^2H and δ^{18}O) and Cl/Br ratio, to improve the understanding of surface-water/irrigation-water/groundwater interactions and (3) nitrate and boron stable isotopes to infer sources and identify controlling processes of nitrate pollution. Mixing models calculated using (1) δ^2H and/or δ^{18}O and (2) Cl/Br are well-known tools able to quantify proportions of the different sources of, respectively, water and salinity (Alcalá and Custodio, 2008; Clark, 2015; Katz et al., 2011; Richards et al., 2018; Solder and Beisner, 2020; Vengosh and Pankratov, 1998). The application of conservative mixing models can be limited by the operation of non-conservative processes (e.g., the degradation of organic matter increases concentrations of bromide with respect to chloride; McArthur et al., 2012), the presence of more than two/three end-members (Phillips and Gregg, 2003), and the variability and uncertainty of the end-members' value (Phillips and Gregg, 2001; Séraphin et al., 2016).

2. Study area

The study area covers ~2000 km^2 within the basin of Oglio River, in the Alpine sector of the Po Plain, N Italy, at the transition between the Alps, to the north, and the alluvial Po basin, to the south (Fig. 1). This area was covered by previous studies (Bartoli et al., 2012; Delconte et al., 2014; Rotiroti et al., 2019a; Zanotti et al., 2019) that described its land use, hydrology, hydrogeology and hydrochemistry, therefore only a brief summary is given below. The plain area has a gentle decrease in elevation (gradient of 0.3–4 m per km) and can be subdivided into two parts: the higher (northern) and the lower (southern) plain (Fig. 1). The transition is marked by a narrow area with numerous lowland springs, i.e., groundwater outflows, that is named "the springs belt" (Fig. 1). The study area is crossed by the Oglio River, that outflows from the subalpine Lake Iseo and receives, along its course, waters from five main tributaries (Fig. 1): the Cherio River, the Scolmatore di Genivolta Channel, the Saverona Stream, the Strone River and the Mella River.

The higher plain hosts a mono-layer unconfined aquifer, at least within the first 100 m of depth, made of sands and gravels, whereas a multi-layer aquifer system, comprised of multiple sand bodies (confined aquifers) intercalated within silt and clay (aquitards), features the lower plain. Groundwater flow is mainly from N to S; in the lower plain, baseflow to gaining rivers imparts strong local variations to the direction of groundwater flow (Rotiroti et al., 2019a). In particular, the Oglio River is losing in its first stretch (i.e., from the outflow from Lake Iseo to approximately 20–30 km downstream) and becomes gaining up to the confluence with Mella River (Rotiroti et al., 2019a). The higher plain aquifer is recharged by (1) local precipitation, (2) irrigation return flow and (3) surface mountain-front recharge. The last is defined by Markovich et al. (2019) as precipitation in mountain slopes that becomes surface runoff, and is then collected in mountain streams/rivers that lose water to the basin aquifer when they exit the mountain area; the Gandovere Stream (Fig. 1) is an example of this type of mountain streams in the study area. The higher plain aquifer discharges through four sinks of groundwater: (1) rivers' gaining sectors, (2) outflow through the springs belt, (3) outflow to the lower plain aquifer and (4) well abstraction (Rotiroti et al., 2019a).

The lower plain aquifer is mainly recharged by the sole inflow from the higher plain aquifer since the widespread presence of shallow confining low-permeability layers prevents infiltration from the surface. The lower plain aquifer discharges through gaining rivers and well abstraction (Rotiroti et al., 2019a).

Concerning hydrochemistry, the higher plain groundwater is oxic and affected by nitrate pollution, whereas the lower plain groundwater is anoxic and affected by arsenic pollution (Rotiroti et al., 2021). Land use in the study area is mostly agricultural, with a dominant corn cultivation for cattle and pig feeding. Agricultural fields are mainly irrigated through surface irrigation methods using two sources of water: (1) Lake Iseo/Oglio River water, distributed through an extensive network of irrigation channels; this surface-water-irrigation is used in the higher plain (Fig. 1); (2) groundwater abstracted through irrigation wells; this groundwater-fed irrigation is used in the lower plain and in the northern part of the higher plain, i.e., the piedmont area, that is not covered by the network of irrigation channels. Surface water used for irrigation is diverted from the losing stretch of the Oglio River and is of good quality, with nitrate concentrations generally below 5–7 mg/L.

3. Materials and methods

3.1. Data

The present work relies on data from 162 water points (Fig. 1, Table S1) divided into two networks: (A) 83 points (56 wells, 8 lowland springs, 1 rainwater collector, 1 lake and 17 river points) monitored

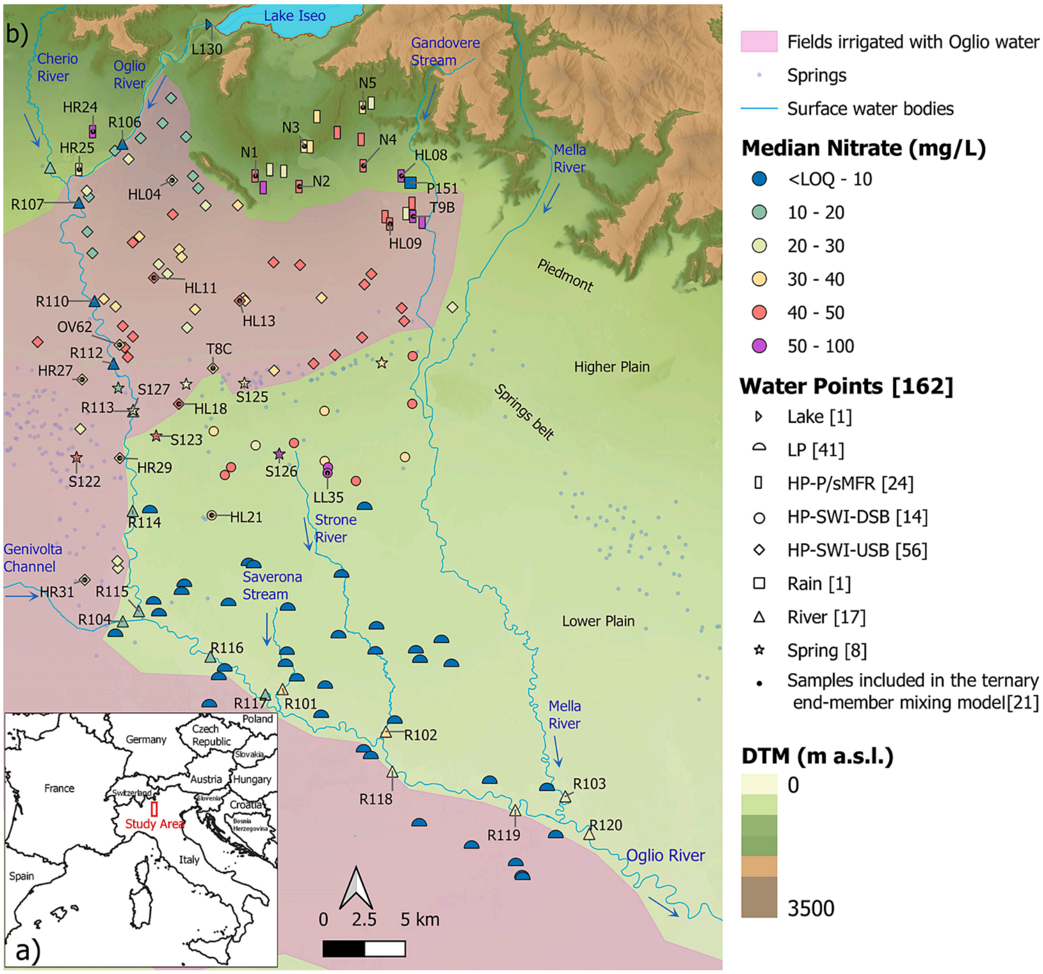

Fig. 1. a) location of the study area. b) map of median NO_3 for all monitoring points grouped according with the classification described in Sect. 3.2. Wells labelled with ID number were sampled for Cl/Br and δ^2H-H_2O (Table S3) and/or $\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3 and $\delta^{11}B$ (Table S4).

between October 2015 and September 2017 by Rotiroti et al. (2019a,b), and (B) 79 wells monitored between 2009 and 2019 by the local drinking water supplier, Acque Bresciane S.r.L. S.B. Data from the network A, a mixture of literature and new original data (Table S2), consist of nitrate and boron concentrations, Cl/Br ratio and stable isotope compositions of water, nitrate and boron. Data from the network B consist of only nitrate concentrations. To supplement network B data, 7 wells mainly located in the piedmont area (N1-5, T8C and T9B) were sampled in March 2022 for boron, Cl/Br and stable isotope analyses (well T8C was sampled for only Cl/Br and water isotopes). Additionally, the Gandovere stream (Sect. 2) was sampled in March 2022. Nitrate and chloride were analyzed by ion chromatography (IC), whereas boron and bromide by inductively coupled plasma mass-spectrometry (ICP-MS); analytical errors were <5%. Water isotopes were analyzed by wavelength-scanned cavity ring-down spectroscopy (WS-CRDS); results were expressed in the standard δ‰ notation vs Standard Mean Ocean Water 2 (SMOW2), and analytical errors were ±1‰ for δ^2H and ±0.2‰ for $\delta^{18}O$. The analyzes of $\delta^{15}N$ and $\delta^{18}O$ in nitrate were performed by isotope ratio mass spectrometry (IRMS) after pre-concentration and purification following Silva et al. (2000); results were expressed in the standard δ‰ notation vs atmospheric N_2, commonly called AIR ($\delta^{15}N$), and vs SMOW2 ($\delta^{18}O$), with an analytical error of ±0.5‰ and ±1.0‰, respectively. Due to its very low nitrate concentration, the rainwater sample was analyzed for nitrate isotopes using the titanium(III) reduction method (Altabet et al., 2019), with an analytical uncertainty of ±0.5 ‰ for both isotopes. Values of $\delta^{11}B$ were determined using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) after sample purification; results are expressed in ‰ vs National Bureau of Standards (NBS) 951 with an analytical error of ±0.4 to ±1‰. Oglio River discharge measurements were done in 3 river sections (R106, R114 and R119; Fig. 1) during 7 surveys from 2015 to 2017 (October 2015; February, June and September 2016; March, June and September 2017) using an acoustic doppler current profiler (ADCP).

3.2. Data processing

A stepwise classification was performed to create groups of sampled wells with distinctive hydrogeological features. Firstly, all wells were classified by the type of tapped aquifer, i.e., mono-layer unconfined oxic aquifer in the higher plain or multi-layer confined anoxic aquifer in the lower plain. The type of tapped aquifer was assessed by (a) the comparison between well screen intervals and lithologs to check the presence/absence of confining units above the screens (Zanotti et al., 2022), and (b) the estimation of redox conditions using dissolved O_2 and NO_3 concentrations (strong reducing conditions with O_2 < 2 and NO_3 < 5 mg/L). Secondly, the higher plain wells were classified by the type of dominant groundwater recharge estimated by a ternary end-member mixing model using δ^2H-H_2O and Cl/Br as conservative tracers (Fig. 2). A combination of a tracer of solutes (Cl/Br) and a tracer of the solvent (δ^2H) is able to fully address the origin of the whole solution (Rotiroti et al., 2019a). δ^2H is used since it has a lower kinetic fractionation during evaporation than $\delta^{18}O$ (Clark, 2015). Thirdly, the wells with a dominant recharge by return flow from surface-water-irrigation were classified by their location with respect to the springs belt, i.e.,

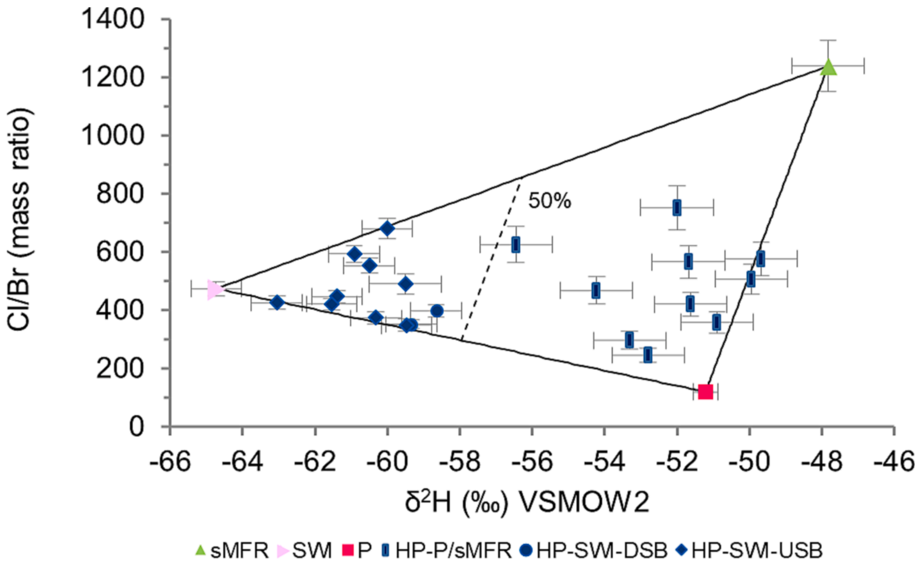

Fig. 2. Plot of Cl/Br vs δ^2H for groundwater samples and mixing lines among end-members of recharge in the higher plain aquifer (see Sect. 3.2 for end-member composition). Error bars represent analytical errors. The percentage label on the mixing lines shows the fractional contribution to mixing of the end-member representing surface-water-irrigation. SWI: surface-water-irrigation. P: local precipitation. sMFR: surface mountain-front recharge. HP-P/sMFR: higher plain wells mainly recharged by local precipitation and/or surface mountain-front recharge; HP-SWI-USB: higher plain wells mainly recharged by surface-water-irrigation and located upstream of the springs belt; HP-SWI-DSB: higher plain wells mainly recharged by surface-water-irrigation and located downstream of the springs belt.

wells upstream of and within the springs belt or wells downstream of the springs belt. A flowchart representing the stepwise classification is reported in Fig. 3.

The ternary end-member mixing model used in the present work improved the previous binary mixing model implemented by Rotiroti et al. (2019a) adding a third end-member representing the surface mountain-front recharge input. The three end-members used in the mixing model were: (1) rainwater collected in point P151, with δ^2H and Cl/Br mass ratio of -51.2‰ and 119, respectively (Rotiroti et al., 2019a), as a proxy of local precipitation; (2) Lake Iseo water (point L130), with δ^2H and Cl/Br mass ratio of -64.7‰ and 474, respectively (Rotiroti et al., 2019a), as a proxy of surface-water-irrigation; (3) Gandovere Stream water, with δ^2H and Cl/Br mass ratio of -47.8‰ and 1238, respectively, as a proxy of surface mountain-front recharge. Only 21 out of 94 higher plain wells, i.e., those having Cl/Br (mg/L) and δ^2H (‰) values (14 samples from Rotiroti et al. (2019a) plus 7 samples collected in March 2022), were plotted in the mixing model diagram

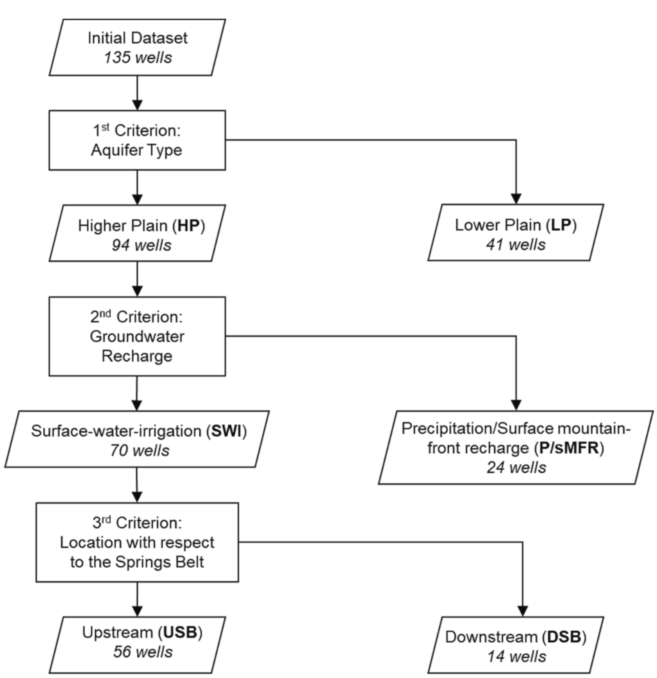

Fig. 3. Flowchart of the stepwise classification of wells.

(Table S3); the remaining 73 wells were classified by analogy (see Sect. 4.1). Relative fractions (f, dimensionless) of the three different end-members for the 21 wells were calculated according with the following equation system (Clark, 2015):

$$f_P + f_{sMFR} + f_{SWI} = 1 \tag{1}$$

$$Cl/Br_w = f_P Cl/Br_P + f_{sMFR} Cl/Br_{sMFR} + f_{SWI} Cl/Br_{SWI} \tag{2}$$

$$\delta^2 H_w = f_P \delta^2 H_P + f_{sMFR} \delta^2 H_{sMFR} + f_{SWI} \delta^2 H_{SWI} \tag{3}$$

where

- P = local precipitation.
- sMFR = surface mountain-front recharge.
- SWI = surface-water-irrigation.
- W = higher plain well.
- and f can be solved using the following equations:

$$f_P = \frac{1 - \frac{Cl/Br_w}{Cl/Br_{SWI} - Cl/Br_{sMFR}} + \frac{Cl/Br_{sMFR}}{Cl/Br_{SWI} - Cl/Br_{sMFR}} - \frac{\delta^2 H_w}{\delta^2 H_{sMFR} - \delta^2 H_{SWI}} + \frac{\delta^2 H_{SWI}}{\delta^2 H_{sMFR} - \delta^2 H_{SWI}}}{1 - \frac{Cl/Br_P - Cl/Br_{sMFR}}{Cl/Br_{SWI} - Cl/Br_{sMFR}} - \frac{\delta^2 H_P - \delta^2 H_{SWI}}{\delta^2 H_{sMFR} - \delta^2 H_{SWI}}} \tag{4}$$

$$f_{SWI} = \frac{Cl/Br_w - Cl/Br_{sMFR} - f_P\left(Cl/Br_P - Cl/Br_{sMFR}\right)}{Cl/Br_{SWI} - Cl/Br_{sMFR}} \tag{5}$$

$$f_{sMFR} = 1 - (f_{SWI} + f_P) \tag{6}$$

Standard errors of relative fractions were calculated using the spreadsheet ISOERROR (Phillips and Gregg, 2001).

4. Results

4.1. Stepwise classification of wells

The first criterion (i.e., aquifer type; see Sect. 3.2 for more details) allowed to separate the total 135 wells into 94 higher plain (HP) and 41 lower plain (LP) wells (Figs. 1 and 3; Table S1). Concerning the second criterion (i.e., groundwater recharge; see Sect. 3.2 for more details), Fig. 2 shows the mixing model diagram with the 21 wells having Cl/Br and δ^2H values; error bars represent the analytical error and its propagation (Bevington and Robinson, 2003). Table S3 reports calculated relative fractions, with respective standard errors, of the three end-members. Ten wells resulted mostly (>50%) recharged by local precipitation and/or surface mountain-front recharge whereas eleven wells had >50% of recharge by return flow from surface-water-irrigation (Table S3). The former are in the northern, piedmont, part of the higher plain (Fig. 1), where irrigation is absent or localized to smaller areas and based on irrigation wells, i.e., groundwater-fed irrigation. The latter are located where surface-water-irrigation, fed by Lake Iseo/Oglio River water, is used (Fig. 1). This fine-constrained spatial distribution of the dominant recharge was used to classify the remaining 73 higher plain wells with no Cl/Br and δ^2H values: those located in the piedmont area were considered to be mainly recharged by local precipitation and/or surface mountain-front recharge (HP-P/sMFR; Figs. 1 and 3); those located in areas where surface-water-irrigation is made using Oglio River water (pink area in Fig. 1) were considered to be mainly recharged by irrigation return flow (HP-SWI; Rotiroti et al., 2019a; Figs. 1 and 3). It is noted the exception of the well group containing HL09 and T9B that was classified as HP-P/sMFR even if it falls within the area irrigated using Oglio River water (Fig. 1); the reason is the non-intensive surface-water-irrigation practiced here, that leads the upgradient P/sMFR recharge to be dominant. The third criterion of the stepwise classification (i.e., location with respect to the springs belt; see Sect. 3.2 for more details) led to classify 14 wells located downstream of the springs belt (HP-SWI-DSB; Figs. 1 and 3) and 56 wells upstream of and within the springs belt (HP-SWI-USB; Figs. 1 and 3).

4.2. Nitrate spatial distribution

Fig. 1 shows the spatial distribution of median nitrate concentrations for each monitoring point classified according with its type (i.e., lake and river points, spring, rain collector, well) and the stepwise classification of wells reported above (i.e., HP-P/sMFR, HP-SWI-USB, HP-SWI-DSB, LP). The full dataset of median NO_3 for each sampling point is reported in Table S1. Fig. 4 reports the boxplot of median NO_3 for the same groups as Fig. 1.

Concerning groundwater, the piedmont wells mainly recharged by local precipitation/surface mountain-front recharge had generally higher NO_3 concentrations with, respectively, median and 75th percentile of 43.0 and 49.8 mg/L (HP-P/sMFR in Fig. 4), so, approximately, one fourth of these wells exceeded the WHO guideline value of 50 mg/L. Moving downgradient with respect to groundwater flow, entering the areas where recharge is mainly due to surface-water-irrigation, NO_3 concentrations in wells considerably decrease, having median and 75th percentile of 34.3 and 41.6 mg/L, respectively (HP-SWI-USB in Fig. 4). Moving further downgradient, just downstream of the springs belt, groundwater NO_3 increases, with median and 75th percentile of 41.0 and 44.5 mg/L, respectively (HP-SWI-DSB in Fig. 4). Concentrations of NO_3 in spring water agree with these higher values, having median and 75th percentile of 36.7 and 48.9 mg/L, respectively (Fig. 4). Finally in the lower plain aquifer, the wells have very low NO_3 concentrations, generally below the LOD (LP in Fig. 4).

River waters have generally lower concentrations than groundwaters, with median and 75th percentile of 15.6 and 20.8 mg/L, respectively (Fig. 4). The detailed evolution of median NO_3 concentration for each monitoring point along the Oglio River is shown in Fig. 5. Median NO_3 is 2.4 mg/L at the outflow from Lake Iseo and increases slightly along the losing stretch of Oglio River, with an increment of 0.06 mg/L per km (from points R106 to R110), reaching 6.8 mg/L at point R110. Then, median concentrations quickly increase along the gaining stretch in the higher plain, with an increment of 0.39 mg/L per km (from R112 to R115), reaching 16.3 mg/L at point R115. Finally, along the gaining stretch in the lower plain median concentrations still rise but less rapidly, with an increment (0.09 mg/L per km from R116 to R120) comparable with that of the losing stretch and reaching 21.4 mg/L at point R120.

4.3. Nitrate and boron isotopes

The full dataset for δ^{15}N and δ^{18}O in nitrate and δ^{11}B is reported in Table S4. The plot of δ^{15}N-NO_3 vs δ^{18}O-NO_3 is represented in Fig. 6 using compositional ranges reported by Martinelli et al. (2018). All samples (i.

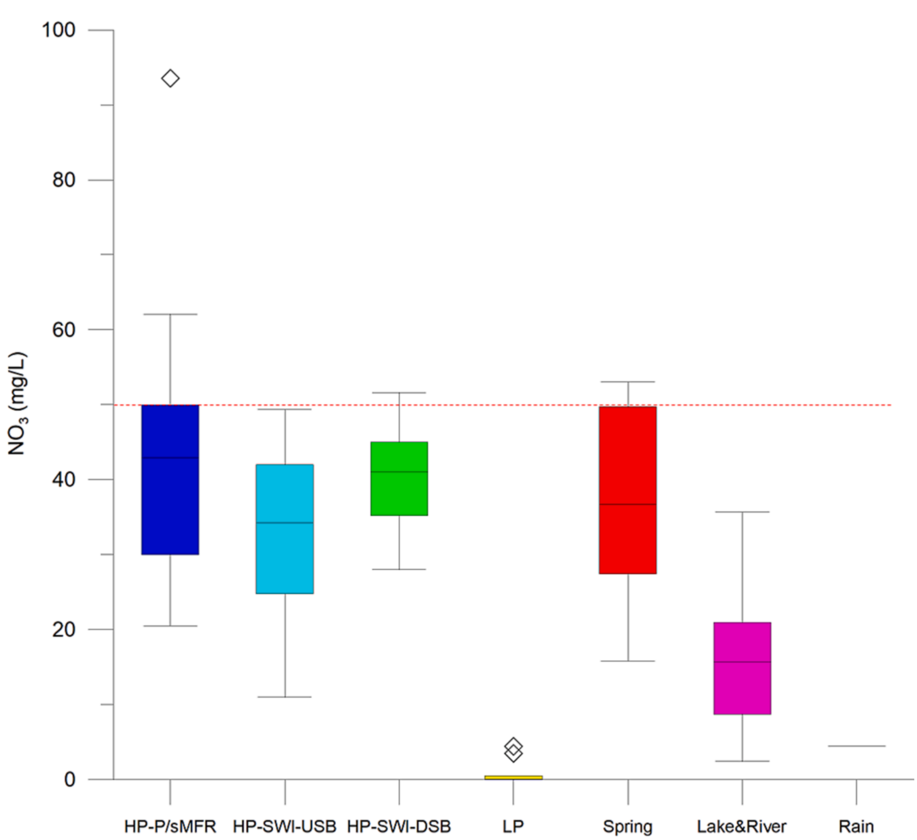

Fig. 4. Boxplot of median NO_3 for the wells grouped by the stepwise classification and for the type of monitoring point. Red dotted line represents the WHO guideline value. HP-P/sMFR: higher plain wells mainly recharged by local precipitation and/or surface mountain-front recharge; HP-SWI-USB: higher plain wells mainly recharged by surface-water-irrigation and located upstream of the springs belt; HP-SWI-DSB: higher plain wells mainly recharged by surface-water-irrigation and located downstream of the springs belt; LP: lower plain wells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

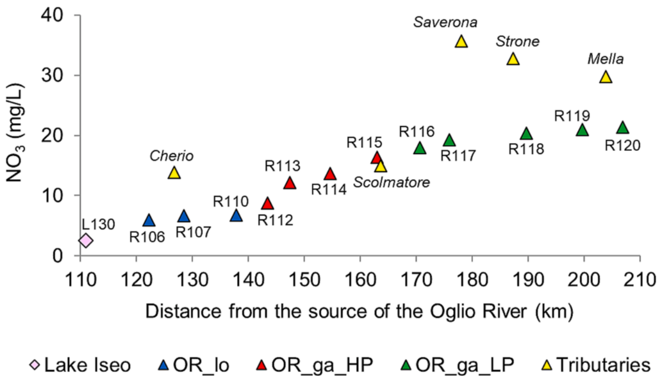

Fig. 5. Median NO_3 concentration for each point along the course of the Oglio River. Labels refer to point IDs. OR_lo: losing stretch of the Oglio River; OR_ga_HP: gaining stretch of the Oglio River in the higher plain; OR_ga_LP: gaining stretch of the Oglio River in the lower plain.

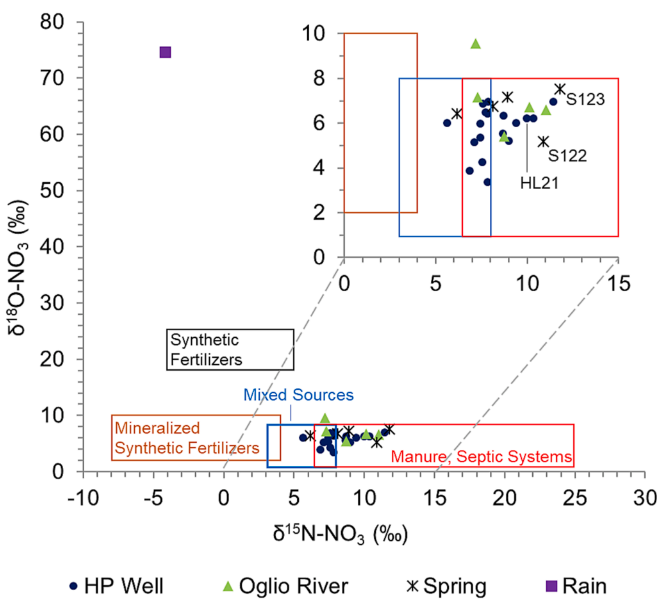

Fig. 6. Plot of $\delta^{18}O$ vs $\delta^{15}N$ in NO_3 for higher plain groundwater, Oglio River, spring and rain samples; compositional ranges are from Martinelli et al. (2018). Labels refer to point IDs mentioned in the text.

e., groundwater, Oglio River and spring waters) fall within a relative narrow range, with $\delta^{15}N$ between 5.6 and 11.8‰ and $\delta^{18}O$ between 4.2 and 9.6‰, corresponding to the compositional ranges of manure/leachate and of natural soil organic nitrogen (Widory et al., 2013). However, due to the high nitrate concentrations largely exceeding natural background levels, values of $\delta^{15}N$ between 3 and 8‰ were not related to natural soils but, instead, to a combined contribution of both manure/leachate and mineralized synthetic fertilizers (Martinelli et al., 2018; Sacchi et al., 2013).

Previous works (Harris et al., 2022; Matiatos et al., 2021; Mengis et al., 2001; Stewart and Aitchison-Earl, 2020) pointed out the role of biogeochemical processes in altering the original isotopic composition of the nitrate source(s). Therefore, it is commonly observed that nitrates leached to groundwater from intensively irrigated agricultural fields have, regardless of the source of fertilizers (i.e., synthetic or animal), a blended isotopic signature around the compositional fields of mixed sourced/soil organic nitrogen, according with the mineralization-immobilization turnover stated by Mengis et al. (2001). This concept considers that the NO_3 in soils, before being leached to groundwater, is subjected to cycles of mineralization and re-incorporation in the organic-N pool, homogenizing its isotopic signature. In this view, the blended isotopic composition of NO_3 found in our samples could support the hypothesis of a main nitrate source to groundwater related to the leaching of NO_3 from agricultural fields. Martinelli et al. (2018), based on a large isotopic database covering the whole Po Basin and including our study area, evidenced that the isotopic signature attributable to nitrification of synthetic fertilizers is not so frequently observed in groundwater. Indeed, the preservation of the isotopic signature of synthetic fertilizers requires not only that they must represent the main N sources applied to agricultural fields, but also a fast transfer of nitrates to groundwater with a low residence time in soils. Moreover, Martinelli et al. (2018) found, at the Po Basin scale, a significant correlation between the median $\delta^{15}N$ values and the number of pigs per Utilized Agronomical Area, whereas no significant correlations could be observed for cattle density, cattle & pig density or population density. Therefore, the positive shift in $\delta^{15}N$ observed in our results could be related to animal husbandry. However, since farm census data are available at the province scale (i.e., approximately the scale of the Oglio River basin), and the number of isotopic data are relatively small, such correlations could not be tested for our study area.

The rainwater sample had $\delta^{15}N$ of −4.2‰ and $\delta^{18}O$ of 74.6‰, that agree with the typical isotopic composition of NO_3 in precipitation (Widory et al., 2013).

Because boron resulted, in general, uncorrelated with nitrate in groundwater (Fig. S1), likely revealing different sources and/or transport mechanisms for these two dissolved species, the $\delta^{15}N_{NO3}$-$\delta^{11}B$ dual isotope approach (Briand et al., 2013; Lasagna and De Luca, 2019; Martinelli et al., 2018) was not used, since the *conditio sine qua non* of a common source and co-migration of B and NO_3 is not met (Leenhouts et al., 1998). The $\delta^{11}B$ vs 1/B plot was used to assess the origin of boron and to trace processes that can also be informative for the understanding of nitrate dynamics (Fig. 7). This plot revealed that wells with significant B concentrations (1/B < 100 L/mg, i.e., B > 10 μg/L) can be classified into three groups, described below. Group (1) collects samples with $\delta^{11}B$ < 10‰, interpreted as groundwater affected by sewage/septic tank effluents, according with the depleted $\delta^{11}B$ characterizing cleaning agents, generally between −10 and 10‰ (Widory et al., 2013). Group (2) contains samples with $\delta^{11}B$ between 10 and 20‰, interpreted as an indication of fertilizers' leaching promoted by irrigation return flow: although fertilizers can have different and variable $\delta^{11}B$ ranges depending on their nature (e.g., synthetic or animal; Widory et al., 2013) and different $\delta^{11}B$ fractionating processes can operate in the soil (e.g., water-clay interaction, bio-uptake by crops), previous works reported narrow ranges of $\delta^{11}B$ in waters leached from agricultural soils, e.g., 11–7‰ by Chetelat and Gaillardet (2005); 10–14‰ by Guinoiseau et al.

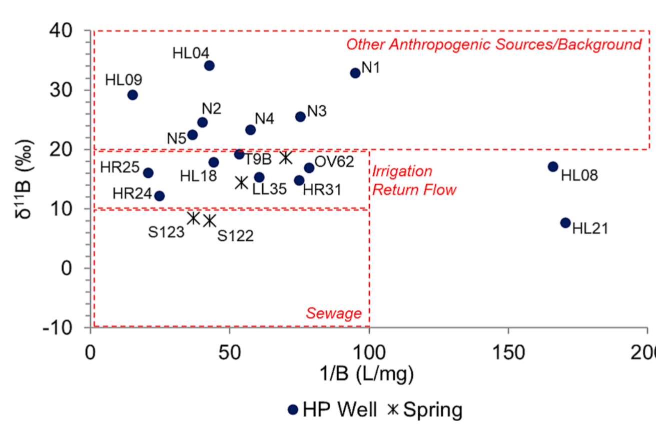

Fig. 7. Plot of $\delta^{11}B$ vs 1/B for higher plain groundwater and spring samples; dotted red boxes represent the three groups described in Sect. 4.3. Labels refer to point IDs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(2018) and 10.6–15.6‰ by Garcia et al. (2021). Group (3) collects samples with $\delta^{11}B$ > 20‰, that may correspond to two types of groundwater: (a) impacted groundwater by various anthropogenic sources, such as organic fertilizers/wastes with enriched $\delta^{11}B$ (Widory et al., 2013), or (b) groundwater with background boron preserving a marine signature, sourced from precipitation (Gaillardet and Lemarchand, 2018) and/or water–rock interaction, such as marine carbonate dissolution (in the range ~20–35‰; Barth, 1993). As for the wells with low B (1/B > 100 L/mg), the well HL08, having the highest NO_3 concentration (median of 93.6 mg/L), may deserve attention. Its low B (6.0 μg/L), with $\delta^{11}B$ equal to 17.1‰, could have two possible explanations: it could be related to (1) the natural background of Po Plain alluvial aquifer, identified by Martinelli et al. (2018) to have $\delta^{11}B$ of 13 ± 2.5‰, or (2) sorption processes in soils during groundwater recirculation associated with groundwater-fed irrigation (see Sect. 5.1 for a detailed discussion).

5. Discussion

5.1. Contrasting impacts of irrigation return flow on groundwater NO_3 concentrations

The piedmont area had the highest groundwater NO_3, as shown in Figs. 1 and 4 (group HP-P/sMFR). Here, agricultural irrigation is not extensively operated or in case it shall be carried out using groundwater (irrigation wells). Values of $\delta^{11}B$ can be used to discriminate between wells affected or non-affected by irrigation return flow (Sect. 4.3). The affected piedmont wells ($\delta^{11}B$ between 10 and 20‰) were HR24, HR25 and T9B, with a median NO_3 of 51.8 mg/L. However, if well HL08 is also included in this group (see Sect. 4.3), median NO_3 increases up to 54.9 mg/L. By contrast, the non-affected piedmont wells ($\delta^{11}B$ > 20‰; n = 6) had median NO_3 of 38.0 mg/L. The one-sided Kolmogorov-Smirnov test (Smirnov, 1939) confirmed (p-value of 0.033) that NO_3 concentrations in the four wells affected by irrigation return flow are significantly higher with respect to those in the six non-affected wells. These data suggest that irrigation return flow, when groundwater is used as irrigation water, generates high NO_3 concentrations in groundwater, that can exceed the WHO guideline value of 50 mg/L. The cause relies on the recirculation of groundwater that promotes NO_3 leaching from soils at each cycle of groundwater infiltration/abstraction. High NO_3 concentrations generated by the recirculation of groundwater due to irrigation were found in other areas worldwide (Brown et al., 2011; Foster et al., 2018; Stewart and Aitchison-Earl, 2020). The evolution of NO_3 vs B concentrations confirms the occurrence of this process. Indeed, NO_3 and B were reported to increase and decrease, respectively, during infiltration of excess irrigation water through agricultural soils, because NO_3 is leached from fertilized soils whereas B is sorbed onto soil clays (Guinoiseau et al., 2018). This relevant negative correlation is also observed in our four affected piedmont wells (r^2 = 0.86; Fig. S2). In this view, the concentrations of NO_3 over B can be considered as a proxy of the intensity of groundwater recirculation: well HL08 seems strongly affected by irrigation return flow whereas well HR25 seems less affected.

As opposite, the area intensively irrigated using Lake Iseo/Oglio River water had lower groundwater NO_3 (group HP-SWI-USB; Figs. 1 and 4). The primary role of irrigation return flow as groundwater recharge input in this area was demonstrated by $\delta^{18}O/\delta^{2}H$ in water and Cl/Br values (Rotiroti et al., 2019a) and is further confirmed here by $\delta^{11}B$, ranging between 10 and 20‰ in wells HL18, HR31 and LL35. High irrigation return flow, when low-NO_3 water is used, generates, after an initial NO_3 spike, lower NO_3 concentrations in groundwater, at the end of the irrigation period, due to dilution. Both (a) excess irrigation water distributed on the field and (b) loosed water from unlined irrigation channels can recharge the aquifer with low-NO_3 water (Rotiroti et al., 2019a). This process was identified in other areas of the Po Plain (Balestrini et al., 2021; Severini et al., 2022) and worldwide (Böhlke et al., 2007; Bouimouass et al., 2022).

5.2. Evolution of nitrate pollution along the hydro-system

Linking the spatial distribution of nitrate concentrations and nitrate/boron isotopes with hydrogeological features, sources of groundwater recharge and agricultural irrigation practices, a general picture on the evolution of nitrate pollution along the studied hydro-system, characterized by a strong groundwater/surface-water/irrigation-water interaction, can be drawn (Fig. 8). Starting from precipitation, a previous study in the nearby area of Milan (Stevenazzi et al., 2020) estimated a relevant amount of total N from atmospheric depositions (between 14 and 30 kg/ha yr) due to anthropogenic emissions. However, in our samples, the NO_3 isotopic signature (Fig. 6) clearly indicated that the precipitation N signature is overwhelmed by that of the terrestrial sources, and therefore that atmospheric deposition contributes negligibly to groundwater and surface water nitrate pollution. Accordingly, the source of nitrate pollution in the study area can be ascribed to a N surplus in soils generated by a N input from agriculture (using both synthetic and animal fertilizers) that is greater than the N crop demand (Bartoli et al., 2012) and, locally, it can be also generated by civil and industrial activities (Sacchi et al., 2013). The $\delta^{15}N$ and $\delta^{18}O$ in nitrate and $\delta^{11}B$ values suggested that the main source of groundwater NO_3 is related to agricultural activities (blended signatures associable to agricultural fields, see Sect. 4.3 for more details), although untreated civil/industrial effluents can generate local hotspots of NO_3 in groundwater (e.g., samples S122, S123 and HL21 with enriched $\delta^{15}N$ and depleted $\delta^{11}B$; Figs. 6 and 7). Moreover, the blended isotopic signatures can be the result of a mixture of different anthropogenic sources accumulated over time both in soil and the aquifer, given the fact that in the area groundwater ages are estimated to be in the order of decades (Musacchio et al., 2018). Generally high NO_3 concentrations in groundwater (25th-75th percentile = 34–50 mg/L) are found in the piedmont area (Fig. 1), the upgradient part of the Po Plain aquifer system, thus indicating that relevant amounts of NO_3 enter the aquifer at the beginning of groundwater circulation and compromise the groundwater quality of all downgradient aquifers. The very high NO_3 in piedmont groundwater (>50 mg/L), i.e., the hotspot, is locally generated by groundwater recirculation due to groundwater-fed irrigation (Sect. 5.1). Moving downgradient, entering the area irrigated with surface water, groundwater NO_3 concentrations are lowered (25th–75th percentile = 26–42 mg/L) by dilution due to the larger recharge flux generated by irrigation return flow. A similar effect of surface-water-irrigation was found by Castaldo et al. (2021) in the San Joaquin Valley (California, USA). The traditional method of surface irrigation using irrigation channels fed by Lake Iseo/Oglio River (i.e., low-NO_3 waters) is an inefficient irrigation technique (around 60% of irrigation water infiltrates down to the aquifer) that significantly recharges the aquifer, as indicated by a groundwater table rise up to 4 m from April (just before the irrigation period) to September (the end of the irrigation period; Rotiroti et al., 2019a). Just downstream the springs belt, groundwater NO_3 increases (25th-75th percentile = 35–45 mg/L) for two main reasons. Firstly, dilution, guided by the return flow, cannot take place here due to a physical limit; as the groundwater table approaches the ground level (the necessary condition for the existence of the lowland springs) it cannot rise further, so the volume of groundwater remains constant and dilution cannot occur; the irrigation return flow generates an increment in springs discharge rather than groundwater table rise. Secondly, no low-NO_3 water is used for irrigation; instead, a mixture of Lake Iseo/Oglio River water, spring water and groundwater (irrigation wells) is used here as the source of irrigation water (ANBI-Lombardia, 2022). Moving further downgradient, entering the anoxic lower plain aquifer, nitrate is rapidly denitrified, so concentrations decrease down to the LOD.

At the transition between higher and lower plain, a change in the type of water body affected by nitrate pollution occurs: from groundwater bodies in the higher plain to surface water bodies in the lower plain (Fig. 8). This transfer of nitrate pollution takes place through (1)

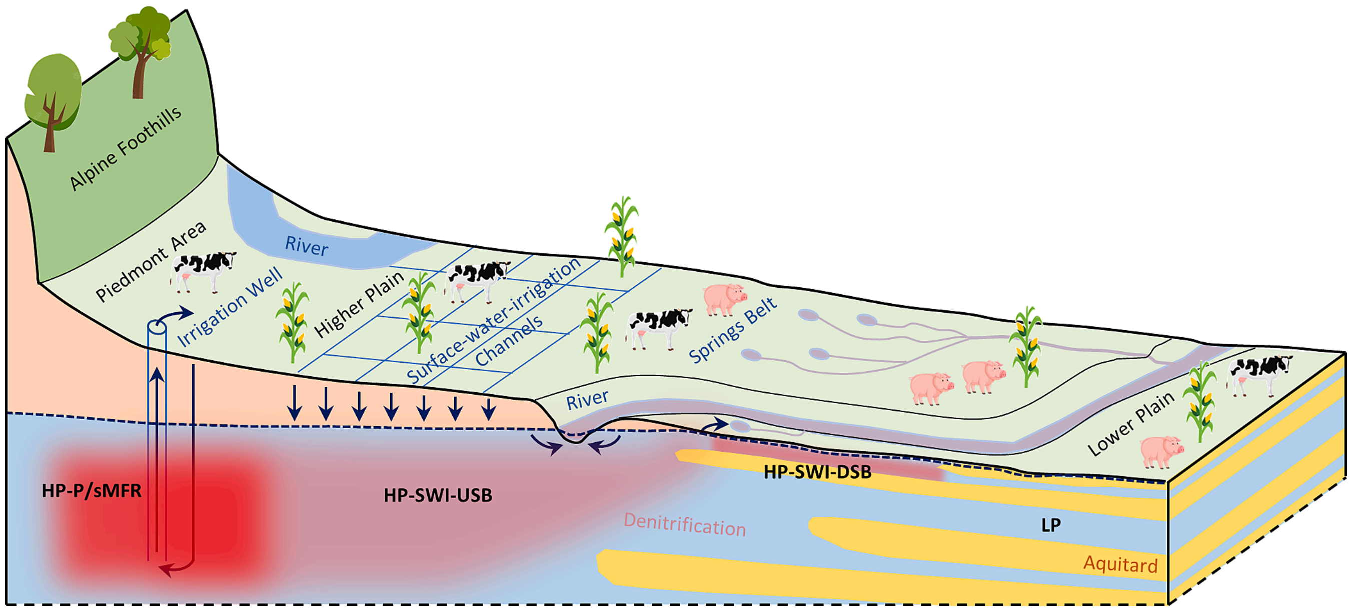

Fig. 8. Conceptual model for the evolution of nitrate pollution along the studied hydro-system. Red color saturation represents the intensity of nitrate pollution in both groundwater and surface-water bodies. HP-P/sMFR: higher plain wells mainly recharged by local precipitation and/or surface mountain-front recharge; HP-SWI-USB: higher plain wells mainly recharged by surface-water-irrigation and located upstream of the springs belt; HP-SWI-DSB: higher plain wells mainly recharged by surface-water-irrigation and located downstream of the springs belt; LP: lower plain wells. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

lowland springs, that are fed by the outflow of the higher plain aquifer and discharge to small lower plain streams (as also evidenced by Balestrini et al., 2021); these in turn, feed larger streams/rivers, such as the Saverona Stream and Strone River, ending up into the Oglio River; (2) gaining rivers in the higher plain, in particular, the gaining stretch of Oglio River, where the steep increase of NO_3 concentrations (Fig. 5) is interpreted as the transfer of nitrate from the aquifer to the river; the strong negative correlation ($r^2 = 0.72$) between river discharge and river NO_3 concentration observed only in the higher plain gaining stretch (Fig. S3) is interpreted as a confirmation that the main nitrate source to the river is the baseflow contribution of groundwater discharge. This process was already evidenced by other studies in the Oglio River watershed (Bartoli et al., 2012; Delconte et al., 2014) and is a common feature of other agricultural basins crossing the springs belt area of the Po Plain (Racchetti et al., 2019).

5.3. *Implication for water management in a changing climate*

It may seem obvious, but the sole effective strategy to mitigate water nitrate pollution in the study area is the reduction of N loads distributed to agricultural soils. The previous study by Musacchio et al. (2021) in the neighboring watershed of Adda River estimated that a reduction by 30% of the N input to soils is needed to meet the goals of the EU Nitrate Directive (EC, 1991). An easy way to reduce the N input from fertilizers could be to count, in the soil N budget, the N input deriving from groundwater nitrate, where groundwater-fed irrigation is done. The use of high-nitrate groundwater ($NO_3 > 50$ mg/L) for irrigation can act as fertigation, requiring lower N input to soils from synthetic/animal fertilizers.

A key aspect that should be considered by water management authorities is that surface water, irrigation water and groundwater are components of the same hydro-system. Thus, future polices for water management/protection should be based on a holistic approach involving all human activities that have a strong connection with water, such as agriculture, tourism, urban life, industry, etc. In this view, it should be considered, for example, that climate change adaptation and mitigation actions facing water scarcity in agriculture also have implications on nitrate pollution of surface-water and groundwater bodies. More specifically, if irrigation using the low-nitrate water of subalpine lakes will be abandoned in favor of groundwater-fed irrigation due to severe summer droughts (such as that of summer 2022), groundwater nitrate concentrations in the higher plain, and consequently surface-water nitrate concentration in the lower plain, will likely increase (and will continue to increase over future years) due to groundwater recirculation, as already happens in the piedmont area. Moreover, even if surface water will be maintained as source of irrigation water but the traditional, and inefficient, method of surface irrigation will be substituted by more efficient methods (e.g., sprinkler, drip, micro irrigation), groundwater nitrate in the higher plain might increase due to the obliteration of recharge by return flow and the consequent dilution effect.

Unfortunately, the substitution of surface-water-irrigation with groundwater-fed irrigation seems quite inevitable in the coming years due to the probable intensification of summer droughts (Baronetti et al., 2022; Polade et al., 2014; Taylor et al., 2013). This observation should foster the discussion among stakeholders about the sustainability of the current N load generated in the Po Plain, mainly by cattle raising activities, and the consequent need to dispose the large amount of animal manure produced (Viaroli et al., 2018). To avoid the consequent aggravation of water pollution by nitrate (due to groundwater recirculation), some adaptation actions should be enforced to compensate the missing recharge made by surface-water-irrigation and to maintain the dilution effect. Managed aquifer recharge (MAR) actions could be performed in rainy, non-irrigation, periods to take advantage of water abundance of rivers under high-flow conditions. A particular MAR system successfully experimented in other areas of the higher Po Plain is the so-called "forested infiltration area" (FIA; Mezzalira et al., 2014; Rossetto and Bonari, 2014). The FIA system consists in channeling surface waters during non-irrigation period into high-permeable fields planted with trees and/or shrubs. Each FIA can be fed by water diverted from rivers and distributed through the existing irrigation channels network. Distributed FIA systems at basin scale may ensure groundwater recharge with surface, low-nitrate, water in rainy periods (typically fall and spring), preserving the dilution of groundwater nitrate in the higher plain and providing, in summer, relatively low-nitrate groundwater to be used for groundwater-fed irrigation, so that the increase of nitrate concentration, intrinsically related to groundwater recirculation, can be mitigated. Future developments should be addressed to implement pilot FIA systems in the study area to test their feasibility and their efficiency in contrasting nitrate increase in groundwater by regular monitoring of groundwater nitrate concentrations.

6. Conclusions

The present work investigated the nitrate pollution affecting a hydrosystem characterized by a strong interaction between groundwater, surface water and irrigation water with the aim of assessing pollution sources, identifying the main processes controlling pollution dynamics and suggesting some pollution mitigation and climate change adaptation strategies. The main outcomes of the study are listed below.

- The main source of the diffuse nitrate pollution is related to agricultural activities; however, untreated civil/industrial effluents can generate, locally, important point-sources of pollution.
- Hydrological processes related to agricultural irrigation have a strong control on nitrate pollution: groundwater-fed irrigation generates high-NO_3 groundwater due to groundwater recirculation, whereas intensive surface-water-irrigation, fed by low-NO_3 water, promotes the decrease of groundwater nitrate due to dilution.
- Nitrate pollution affects groundwater bodies in the higher plain, leaving here surface water bodies unaffected; entering the lower plain, groundwater nitrate is removed by denitrification whereas surface water bodies become affected by nitrate pollution due to the transfer of nitrate loads from higher plain groundwater to steams/rivers via outflow from the springs belt and baseflow to gaining rivers.
- Reducing the N input to soils from fertilizers is the sole mitigation strategy able to solve the problem of nitrate water pollution; taking into account, in the soil N budget, the N input deriving from groundwater nitrate, where groundwater-fed irrigation is done, can help decreasing the quantity of synthetic/animal fertilizers applied to soils.
- Adaptation strategies to climate change facing water scarcity for agricultural irrigation should also consider possible water quality drawbacks: if surface-water-irrigation will be abandoned in favor of groundwater-fed irrigation due to the intensification of summer droughts, groundwater nitrate concentrations are expected to increase due to groundwater recirculation and the cessation of dilution; in order to attenuate this phenomenon, an adaptation strategy might be the implementation, during non-irrigation rainy periods, of managed aquifer recharge works, such as forested infiltration areas, to take advantage of water abundancy from rivers under high-flow conditions, maintaining the dilution effect.

This work demonstrated how a holistic approach, considering the interactions between groundwater and surface-water and, eventually, irrigation water, is of fundamental importance when dealing with the pollution of freshwater resources, contributing to the sustainable management of their quality and quantity.

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CRediT authorship contribution statement

Marco Rotiroti: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Elisa Sacchi:** Conceptualization, Methodology, Writing – review & editing. **Mariachiara Caschetto:** Investigation, Visualization, Writing – review & editing. **Chiara Zanotti:** Investigation, Data curation, Writing – review & editing. **Letizia Fumagalli:** Resources, Supervision, Funding acquisition. **Michela Biasibetti:** Resources, Writing – review & editing. **Tullia Bonomi:** Resources, Writing – review & editing, Supervision, Project administration. **Barbara Leoni:** Resources, Supervision, Funding acquisition, 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 are available in the supplementary material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2023.129868.

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