Agricultural practices regulate the seasonality of groundwater-river nitrogen exchanges

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Abstract

Soil system budgets are generally performed aggregating annual nutrient inputs and outputs over arable land to infer their use efficiency and water pollution risk in watersheds with intensive agriculture and animal farming. They are seldom partitioned into seasonal budgets and matched with seasonal transport of nutrients in adjacent river reaches. In this work we calculated seasonal soil nitrogen (N) budgets in a Mincio River sub-basin (Northern Italy), and we analyzed the dissolved inorganic N net export in the river reach draining such sub-basin. Our results suggest pronounced seasonal differences of soil system budgets with N excess in winter and even more in spring, equilibrium among sources and sinks during autumn and N deficit during summer. Seasonal inorganic N loads transported by the river were not correlated with soil system budgets as they peaked in late summer and were at their minimum in early spring. Fertilization uncoupled to significant uptake supports N excess in winter and spring, whereas crop uptake uncoupled to N inputs supports summer N deficit. Within the river reach potential nitrification cannot explain nitrate accumulation in the water, suggesting alternative dynamics, related to the seasonality of irrigation practices, driving the local hydrology. Flood irrigation results in large soil nitrate solubilization, horizontal and vertical transport and in upward vertical migration of the groundwater piezometric head during the spring and the summer. River water is likely replaced by nitrate-rich groundwater when the groundwater recharge exceeds a certain threshold coinciding with late summer. Irrigation is then interrupted and the piezometric head, together with nitrate exchange, decreases. This work suggests that a deep understanding of N dynamics in watersheds with intensive agriculture and animal farming and irrigation via flooding on permeable soils needs the implementation of hydrological studies and the reconstruction of the vertical pathways of nitrate and of river-groundwater interactions. Moreover, the partitioning of annual into seasonal N budgets and their combination with irrigation practices allows the identification of hot moments in N cycling. Agricultural practices minimizing nitrate excess, its mobility and the risk of ground and surface water pollution are suggested for this area.

1. Introduction

The dramatic increase of anthropogenic reactive nitrogen (N) inputs in watersheds with intensive agriculture and animal farming has demonstrated negative effects for inland water and groundwater chemical and biological quality, drinking water supplies, ecosystem integrity and functioning and human health (Van Grinsven et al. 2006; Galloway et al. 2008; Rivett et al. 2008; Schlesinger, 2009; Sobota et al. 2015; Huang et al. 2017). Such negative effects are amplified by the human-derived alteration of the hydrological cycle at the watershed scale and by climate change (Galloway et al. 2008; Overeem et al. 2013; Woolway and Merchant, 2019; Woolway et al. 2020). Among the underlying mechanisms are water abstraction for irrigation or industrial purposes or climate change-related drought reducing river discharge and its capacity to dilute and process N loads (Palmer et al. 2008). Low discharge promotes also hyporheic anoxia and ammonium recycling from sediments (Hlaváčová et al. 2005). Hydrological extremes include also short-term, heavy precipitations resulting in high discharge events transferring large N loads from cultivated areas saturating riverine denitrification capacity (Viaroli et al. 2018; Magri et al. 2019).

Nitrogen budgets calculated for agricultural soils within a river basin allow to evaluate the potential risk of diffuse N pollution (Oenema et al. 2003; Soana et al. 2011). In agricultural soils, N inputs associated with organic or synthetic fertilizers, atmospheric deposition or biological fixation can be either temporarily retained

in crops or released to the atmosphere as gaseous losses. Nitrogen inputs in excess to temporary retention or permanent loss can be transferred via runoff to adjacent aquatic ecosystems (Howarth et al. 1996; Seitzinger et al. 2006; Pinardi et al. 2018, 2020). If soil system budgets in arable land produce reliable snapshots of N pools and fluxes in cultivated areas, the detailed reconstruction and partitioning of N pools and fluxes within watersheds is a challenging objective. For example, seasonally variable water inputs to agricultural soils via precipitation and irrigation affect soil N leaching, horizontal and vertical transport and transformation, N use efficiency as well as river-groundwater interactions and associated N exchange (Schaefer and Alber, 2007; Howarth et al. 2012; Sinha and Michalak 2016). Moreover, in intensively cultivated floodplains the hydrological cycle has been regulated by the realization of infrastructures as dams and networks of canals that help buffering climatic anomalies and ensure water availability for crops. In Italy for example, the Alpine sector of the Po River basin hosts large dams that regulate the release of water from deep subalpine lakes (Maggiore, Como, Iseo, Idro and Garda Lakes) to their emissaries (Ticino, Adda, Oglio, Chiese and Mincio Rivers). Winter water retention in subalpine lakes occurs at the cost and drawbacks of reduced water discharge and contributes to the downward vertical migration of groundwater, often resulting in downwelling river-groundwater interactions (i.e. the river feeds the groundwater) (Rotiroti et al. 2019; Severini et al. 2021). On the contrary summer irrigation, besides representing a vehicle for N transport, produces opposite effects, often reversing the direction of river-groundwater interactions (i.e. upwelling, the groundwater feeds the river). These practices, that characterize anthropogenic, intensively cultivated, and hydraulically regulated watersheds with permeable soil, introduce marked seasonality in N budgets (Lin et al. 2019; Racchetti et al. 2019).

Many authors reported a significant correlation between annual N input to croplands and river N export (Neff et al. 2003; Yan et al. 2010; Xu et al. 2013; Strokal et al. 2014; Tong et al. 2017), but they did rarely account for the seasonality of N input and export (McCrackin et al. 2014; Chen et al. 2019). Studies targeting N budgets in agricultural watersheds are generally conceived at the annual scale for mainly practical reasons, as agricultural census data are collected and published by national statistical institutions with annual frequency. Such an approach from one side allows to calculate N use efficiency in cropland and potential N loss, but from the other side, it misses temporal resolution and precludes the understanding of seasonal variations of the array of N-related processes, potentially regulated also by climate change. For example, human activities (e.g., crop production) and altered hydrology may influence the seasonality of N river export (Basu et al. 2010; Compton et al. 2020), together with the seasonal evolution of temperature that influences N losses, retention and removal processes (e.g., denitrification) (McCrackin et al. 2014). Understanding how seasonal variations in human activities and hydrology influence N budgets in agricultural soils and N transport by rivers is important to better understand the mechanisms underlying N transformations along the terrestrial-aquatic path, improve agricultural practices to increase N use efficiency and decrease N pollution, and eventually forecast how climate change will affect N dynamics (Mas-Pla and Menció, 2019). This important set of objectives is a difficult target at the scale of whole watersheds due to scarce resolution of available data and spatial heterogeneity (e.g. pedology, land use, etc). Smaller scales of analysis, targeting specific and homogeneous river and watershed sectors, seem much more promising (McCrackin et al. 2014; Chen et al. 2019; Compton et al. 2020).

Different studies carried out at large temporal and spatial scales (Soana et al. 2011; Pinardi et al. 2018; Viaroli et al. 2018; Lassaletta et al. 2021) have highlighted the presence of hot-spots within watersheds that represent outliers in N budgets (e.g., with very large N excess or very low N use efficiency). They also emphasized the

presence of hot-moments within watersheds, that are specific periods during which N mass transfer peaks as a combination of decreased uptake, increased runoff or variation of the water table level, resulting in the reactivation of river-groundwater interaction (Rosenzweig et al. 2008; Preisendanz et al. 2020; Taherisoudejani et al. 2018). The analysis of N hot-spots and hot-moments in watersheds require specific studies, focusing on small spatial and temporal scales.

In Northern Italy, the Po River valley is an alluvial plain heavily exploited by human activities such as agriculture, animal farming, industry, and tourism. Land use change and hydrological alterations determined high pressure on both surface and groundwater (May, 2013; Pérez-Martín et al. 2014; Lasagna and De Luca, 2019) and a wide portion of the plain is classified as vulnerable to nitrate pollution (Martinelli et al. 2018). The main aim of this study is to analyze the seasonal evolution of dissolved inorganic N loads in a fluvial segment of the Mincio River, a tributary of the Po River, characterized by natural banks, gravel bottom with submerged vegetation, and regulated discharge. This segment crosses a transitional area between permeable and non-permeable soils, characterized by springs and classified as an area of river-groundwater interactions (Balestrini et al. 2021). Due to its hydrogeological features and the large water availability, the considered sub basin is a hotspot of intensive agriculture and animal farming and represents a key study area to analyze if and how the seasonality of agricultural practices affects N dynamics.

In this sector of the Po River, groundwater in the phreatic and shallow aquifer has a short residence time as compared to semiconfined or confined deeper aquifers. This is supported by fast (few days) surface-groundwater dynamics of micro-pollutants (Balderacchi et al. 2016) and low concentrations of total dissolved solids (Martinelli et al. 2018). Results of Balderacchi et al. (2016) suggest also fast response of shallow aquifers to changing conditions; as such they allow to trace agricultural practices (e.g., use of herbicides or fertilization) and they respond quickly to hydrologic variations (e.g., drought, precipitations, irrigation). It can be assumed that macrocontaminants as nitrates undergo the same fast transfer mechanisms, also due to their elevated solubility and absence of interaction with soil and sediment.

The main hypotheses of this work are that river-groundwater interactions affect N transport in specific river sectors and vary seasonally due to combination of irrigation practices and inorganic nitrogen excess in soil. We also hypothesized that the seasonal dynamics of such variable interactions can be captured analyzing comparatively seasonal N budget in agricultural soils and seasonal riverine N transport.

2. Study Area

The Mincio River (~75 km) originates from the Lake Garda, the largest Italian Lake, and is a tributary of the Po River (Fig. 1). The hydrological regime of the Mincio River is regulated upstream by a dam, which controls the water discharge from the Lake Garda. Along the river course, a series of dams and weirs feeds a network of canals for irrigation and industrial purposes and controls discharge variations to avoid the flooding of cities and villages. Water management for Lake Garda recreational activities and for agricultural purposes results in marked flow variations. Indeed, since the establishment of the river regulation in the 60's of the last century, the Mincio River discharge averaged ~80 and ~ 30 $m^3 s^{-1}$ during the irrigation (May to September) and outside the irrigation periods, respectively (Lombardy Region, 2006). More recently, projections of decreasing water availability resulted in a further reduction of the Mincio River discharge to ~14 $m^3 s^{-1}$ (www.laghi.net) in

autumn and winter to keep water in the Lake Garda and guarantee water availability for irrigation and tourism in the summer season. During winter, the flow reduction and absence of irrigation result in a decreased aquifer recharge, a phenomenon described by different authors in this geographical area at regional (Rotiroti et al., 2019) and local scales (Severini et al., 2021) and, consequently, in a lowering of the phreatic surface. This water transfer dynamic results in a decrease of groundwater upwelling in winter and early spring (Balderacchi et al. 2016).

A wide segment of the Mincio River, including the portion investigated in this study, flows in a flood plain characterized by a multilayered aquifer system with a cyclic facies architecture mainly made of fluvial-channel (gravel and sand) and floodplain (clay) deposits (Amorosi et al. 2008). As a result, the northern part of the plain (high plain) is locally characterized by shallow phreatic aquifers, while in the southern part (low plain) the floodplain facies act as aquitards or aquicludes, resulting in confined and semi-confined aquifers (Chelli et al. 2018). The river reach investigated, from S1 to S2 (length 8.1 km, mean depth ~ 1 m, mean water velocity ~ 1.0 m s^{-1}) is in the high-medium plain of the Mincio watershed and includes four municipalities (1- Valeggio sul Mincio, 2- Volta Mantovana, 3- Goito, and 4- Marmirolo) for a total surface of 184 km^2 (Fig. 1). Since 2006, these municipalities are classified as Nitrate Vulnerable Zones (NVZs) according to the European Nitrate Directive (91/676/CEE). The study area is characterized by fertile soils due to calcareous gravel deposits and is intensively exploited by agriculture (Utilized Agricultural Area - UAA covers 76% of the study area; Fig. 1) and animal farming (1.2 and 0.6 t of live weight per hectare for cattle and pigs, respectively). The S1-S2 river segment flows into natural banks, has a mainly gravel bottom, and has transparent waters. The main primary producers are submerged vegetation (e.g., *Vallisneria spiralis*) with associated epiphytes, benthic biofilms and different emergent macrophytes growing along the river banks or forming islands (Pinardi et al., 2009, 2014). The linear development of irrigation canals in S1-S2 river reach sub basin sums ∼560 km (Fig. 1). The surface covered by the other aquatic environments, such as quarry lakes is ∼0.62 km^2.

3. Material And Methods

3.1. Nitrogen budgets and water inputs

A comprehensive input–output N budget across the Utilized Agricultural Area (UAA) was compiled by using locally-derived data on farming activity, agronomic coefficients and atmospheric deposition. Nitrogen budget was first calculated at the municipal scale, i.e., the administrative level at which official agricultural statistics are available, then weighted for the percentage of each municipality surface included within the study area, and finally summed up. Census data were integrated in a nutrient budgeting approach proposed by Oenema et al. (2003), recently reviewed by Zhang et al. (2020), and formerly applied to the whole Mincio River basin (Pinardi et al. 2018). Four inputs of N to the UAA were considered (land application of livestock manure, land application of synthetic fertilizers, atmospheric deposition, and biological fixation by crops), together with four outputs of N from UAA (crop harvest, crop stock, ammonia volatilization and denitrification in soils). The difference between N inputs and outputs results in a net, which represents a condition of equilibrium, surplus or deficit of N across the UAA.

The Soil System Budget (SSB) was calculated as follow:

$$SSB\ N = N_{Man} + N_{Fert} + N_{Fix} + N_{Dep} - N_{Harv} - N_{stock} - N_{Vol} - N_{Den}$$

where:

N_{Man} = N in livestock manure applied to agricultural soils

N_{Fert} = N in synthetic fertilizer applied to agricultural soils

N_{Fix} = agricultural N_2 fixation associated with N fixing crops

N_{Dep} = atmospheric N deposition on agricultural land

N_{Harv} = N exported from agricultural soils with crop harvest

N_{stock} = organic N in crop's standing stock

N_{Vol} = NH_3 volatilization in agricultural soils

N_{Den} = denitrification in agricultural soils

All budget terms were expressed in unit of mass per time (t N y^{-1}), and on a per-area basis, after normalization for the UAA (kg N ha^{-1} y^{-1}). The calculation was based on agriculture and farming data for the year 2015 reported by the Agricultural Information System of Lombardy Region (SIARL, www.siarl.regione.lombardia.it) and by the Annals of Agrarian Statistics, published yearly by the National Institute of Statistics (ISTAT, http://agri.istat.it/). SIARL databases, retrieved from the Open Data portal of the Lombardy Region (https://dati.lombardia.it/), provided data for livestock density and agricultural areas at the municipality level, whereas the database of the Annals of Agrarian Statistics provided data for crop yield and fertilizer application (http://dati.istat.it/) at the provincial level. Inputs and outputs were initially calculated for each municipality and then aggregated at the study area level.

Uncertainty in N budget calculations was assessed by a Monte Carlo analysis using Excel and R software (R Core Team 2019). All coefficients used to convert census data into N amounts were assumed to vary stochastically and independently around the average value with a normal probability distribution. For each simulation, a set of coefficients was randomly generated from probability distribution functions and a total of 1000 simulations were run. Budget calculation was conducted both at the annual and at the seasonal scales and compared with seasonal in-stream N loads. Details about annual budget equations, seasonal calculations and sources of census data and agronomic coefficients are presented in Supplementary Material A.

The N loads produced by the urban areas were not included in the calculation because more than 95% of the sewers in the study area are connected to wastewater treatment plants (WWTP). Nearly 75% of the N inputs to WWTP is removed via denitrification in tertiary treatment (Lombardy Region, 2017). Indeed, the calculation of the urban load produced by the resident population, obtained by the conversion of equivalent inhabitant in kg of N per day, resulted in less than 2% of the total N input by diffuse sources (Pinardi et al., 2018).

The daily precipitation data were downloaded from the ARPA Lombardy website (https://www.arpalombardia.it/Pages/Meteorologia/Richiesta-dati-misurati.aspx) at Ponti sul Mincio station (Fig. 1) for the period from 2010 to 2017. The mean annual, seasonal (irrigation and non-irrigation period) and monthly precipitation data were calculated. Irrigation data at the municipality level was obtained from the 6th Agricultural Census (National Institute of Statistics, 2010, http://dati-censimentoagricoltura.istat.it) and then aggregated at the study area level.

3.2. Water sampling and analyses

Two stations located at the extremes of the identified river reach (S1 and S2; Fig. 1) were sampled for water analyses. The two stations were selected as they were located upstream and downstream the area where the Mincio River can be considered as a gaining river in groundwater-surface water interaction, that is the river is fed by groundwater (Racchetti et al. 2019). Given the constant discharge between S1 and S2, the identified river reach was more recently characterized as a flow-through reach (Severini et. al. 2022), with groundwater feeding the river in the western bank and being fed by the river in the eastern bank. Field campaigns were carried out seasonally with a series of daily cycles of repeated samplings carried out on 12–13 August and 15–16 November 2016, 14–15 February, 12–13 April and 13–14 June 2017. Water samples were taken in three replicates every 4 hours for a 24-hour period. An aliquot was transferred into a 12 mL exetainer (Labco, UK), added with 100 µL of $HgCl_2$, and analyzed for dissolved inorganic carbon (DIC) with Gran titration (0.1 N HCl) within 24 hours from sampling. DIC was measured as it may trace differences between surface and groundwater chemistry. Water aliquots were filtered (GF/F glass fiber filters) and transferred to plastic vials for nitrate (NO3-N), nitrite (NO2-N), and ammonium (NH4-N) determination by spectrophotometric methods (Rodier, 1978; APHA, AWWA, WPCF, 1999). Hourly or daily water flow data were obtained by the Interregional Agency for the Po River (AIPO), and by the Mincio Consortium for Pozzolo and Goito sites.

The Mann-Whitney Rank Sum Test was used to test the difference between upstream and downstream values of water flow, NO3-N, NO2-N, NH4-N and DIC concentrations. The R software package (R Development Core Team, 2019) was used to perform all statistical tests.

3.3. Dissolved inorganic nitrogen and carbon daily loads

For each sampling date, daily NO3-N, NO2-N, NH4-N and DIC riverine loads transported at S1 and S2 (kg d^{-1}) were calculated multiplying concentrations by river discharge. The difference between loads at S2 and S1 was calculated according to the following equation:

$$\Delta NO3\text{-}N \text{ (or NO2-N, NH4-N, DIC)} = \sum [Ct \times \Delta t \times Q]_{S2} - \sum [Ct \times \Delta t \times Q]_{S1} \quad (1)$$

where: Ct = concentration of NO3-N (or NO2-N, NH4-N, DIC) at time t downstream (S2) or upstream (S1) (mg m^{-3}); Δt = time interval between samplings (h); Q = water flow (m^3 h^{-1}). Such difference can be null, suggesting equilibrium between inputs and outputs, negative, suggesting net retention or dissipation (e.g., uptake or denitrification), or positive, suggesting the occurrence of production or additional inputs along the stretch (e.g., nitrification or point and diffuse inputs). A standard deviation was associated to NO3-N, NO2-N, NH4-N and DIC measurements made in replicates. The errors conveyed through the mathematical description were calculated with classical error propagation equations.

4. Results

4.1. Nitrogen budgets and water inputs

In the four municipalities under study, the total N inputs to arable land (6010 ± 498 t y^{-1}) were mainly due to livestock manure (59%). Nitrogen outputs (5078 ± 494 t y^{-1}) accounted for 84% of the N inputs and were mainly due to crop harvest (50% of the total N outputs). The main cultivated crop is maize (63% of arable land) followed by permanent grassland. The difference between N inputs and outputs denoted a N soil surplus (932 ± 702 t y^{-1}). The mean areal N surplus was 67 ± 50 kg ha^{-1} y^{-1} with values calculated for the different municipalities ranging between − 172 and 204 kg ha^{-1} y^{-1}. All these results are reported in Supplementary material B, Table B.1 and Figure B.1.

The seasonal SSB is reported in Fig. 2. Manure N fertilization was higher in spring (1590 ± 268 t) and summer (883 ± 149 t), and similar in autumn and winter (530 ± 89 t). Synthetic N fertilization was higher in spring (769 ± 190 t) and winter (257 ± 63 t). Biological N fixation was higher in summer (559 ± 259 t) and spring (350 ± 162 t) whereas atmospheric N depositions were concentrated mainly in summer and autumn (32 ± 4 and 38 ± 4 t, respectively). In spring, N associated to the crop's standing stock (487 ± 98 t) was higher than N in the crop harvest (398 ± 80 t). With respect to N outputs, crop harvest was highest in summer (1492 ± 301 t) and autumn (637 ± 128 t). Ammonia volatilization and soil denitrification were quantitatively important in spring (324 ± 233 t and 210 ± 102 t, respectively). Coupling the seasonal input and output data, a transition from N deficit to N surplus is evident moving from summer (-971 ± 472 t) to spring (1317 ± 464 t).

During the 2010–2017 period the mean annual precipitation in the study area was 910 ± 197 mm y^{-1}, of which about 43 ± 6% occurred during the irrigation period (Fig. 3).

During the May-September period a water volume of 53.3 x10^6 m^3 was used to irrigate 13,513 ha of UAA, which represent 75% of the total arable land. Flooding and sprinkler were the main irrigation typologies (72% and 27% of the irrigated surface, respectively) (data from the National Institute of Statistics).

4.2. Water physico-chemical features of sampling sites

Nitrate and DIC concentrations were significantly higher at the downstream site for all sampling dates (Mann-Whitney Rank Sum Test, $p < 0.001$, $n = 68$ for each parameter; Fig. 4). On the contrary, the concentrations of the other dissolved inorganic forms of nitrogen (NO2-N and NH4-N) were significantly higher at the upstream site ($p < 0.001$, $n = 68$ for each parameter; Fig. 4). The highest NO3-N and DIC concentrations were measured in June 2017 at both sampling sites (1.6 and 3.0 mg NO3-N L^{-1}, and 33 and 41 mg DIC L^{-1} at S1 and S2, respectively). The highest values of NO2-N were recorded in summer at S1 and S2 (up to 101 and 31 μg L^{-1}, respectively), whereas NH4-N concentrations peaked in August 2016 at S1 (up to 122 μg L^{-1}) and were high at both sites in February 2017. Nitrate was always the main form of inorganic nitrogen, accounting on average for 88% and 98% of the total N at S1 and S2, respectively.

The mean annual water flow was 10.3 ± 2.5 m^3 s^{-1} in the S1-S2 river reach (whole dataset 2016–2017, $n = 140$). During the irrigation period the water flow was not significantly different upstream and downstream (11.7 ± 2.0 m^3 s^{-1} at S1 and 13.0 ± 3.9 m^3 s^{-1} at S2; $p > 0.05$). No significant differences were also found

between water flow during the irrigation and not-irrigation periods ($p > 0.05$, $n = 34$). The water discharge measured during the experimental activities fell within the annual range of flow variation.

4.3. Dissolved inorganic nitrogen and carbon daily loads

In all seasons, NO3-N and DIC transported loads were higher at S2, whereas NO2-N and NH4-N loads were higher at S1, but by much lower extent (Fig. 5). A positive correlation was found between NO3-N and DIC concentrations (Pearson's correlation coefficient $r = 0.899$, $p < 0.001$, $n = 68$ for each parameter) supporting the possibility of the same origin for the two solutes. A similar seasonal trend was detected for DIC and NO3-N accumulation along the analyzed river reach (Fig. 5). The maximum increase of transported loads (nearly 11,000 and 1500 kg d^{-1} for DIC and NO3-N, respectively) was measured in August 2016, whereas the minimum increase (nearly 2,000 and 200 kg d^{-1} for DIC and NO3-N, respectively) was measured in April 2017 (Fig. 5). The highest NO2-N and NH4-N loads reduction along the stretch were recorded during summer months (Fig. 5).

5. Discussion

5.1. The seasonality of soil N budgets

Previous studies carried out in the Po River basin and in other geographical areas characterized by intensive agriculture and animal farming suggest a generalized N surplus and inefficient N use, leading to large N losses to surface and groundwater (Soana et al. 2011; Hou et al. 2015; Özbek et al. 2015; Viaroli et al. 2018; Häußermann et al. 2020). In the Po River plain, to our knowledge, only a few sub-basins (e.g., Ticino and Po di Volano) represent exceptions to this rule due to very limited animal farming and synthetic fertilizers inputs balanced with crop needs (Racchetti et al. 2019; Soana et al. 2021). All those studies were carried out on an annual temporal scale, that potentially masked marked seasonal differences. Our calculations suggest a clear seasonal variation in N soil budgets, changing along seasons with periods with deficit (summer), equilibrium (autumn), moderate (winter) or large (spring) excess. These differences arise from variable seasonal balance among agricultural practices, such as large spring manure and synthetic fertilizer spreading uncoupled to crop uptake, moderate spread of fertilizers during winter with little to no uptake or large summer crop uptake in excess to N inputs (Chen et al. 2019). The N assimilation term is calculated as the product of the standing stock by the biomass-specific uptake rates and peaks in summer. Indeed, the biomass-specific uptake tends to decrease along with the crop's growth, but the crop's standing stock is much smaller in spring than in summer. Large spring N inputs are therefore coupled to relatively low uptake, resulting in a maximum surplus, exceeding that calculated for winter, when uptake is minimum. Large summer uptake on the contrary exceeds inputs and results in a seasonal deficit of N in the soil system budget. High fertilization is probably driven by the N need of the main cultivated crop, i.e., maize, which is a water and N-demanding species (FAO, 2006). These results on intra-annual variations in N mass budgets support the relevance of seasonal studies in highlighting critical moments in terms of potential water pollution (Lin et al. 2019; Compton et al. 2020). As nitrate water pollution is correlated with N excess in soils, our outcomes indicate a maximum nitrate pollution risk in the spring, a minimum risk in the summer and something intermediate in winter and autumn. Results from seasonal river N transport suggest something different as the highest N accumulation along the stretch was measured in

summer and the lowest in spring. Taken together, these apparently contrasting results indicate that more factors are involved in the horizontal transfer of soil N excess to surface water and that such factors determine a temporal lag. In the perspective of efficient N use at the soil level, our results stress that the spring is a critical season that requires a thorough re-thinking of practices by better balancing crops needs with fertilizers inputs. During spring, organic and synthetic N inputs need to be better balanced with N uptake, as the crops have high potential growth but low biomass, which results in an insufficient uptake of the large N inputs (Robertson and Vitousek, 2009).

5.2. The seasonality of inorganic N loads in the Mincio River

Results from this work add to a few seasonal studies coupling land mass budgets of N and net river N export-retention (e.g., Chen et al. 2019; Lin et al. 2019; Compton et al. 2020). For the portion of the Mincio River considered in this study, Fig. 6 reports the monthly water inputs, either from precipitation or irrigation, the seasonal soil system N budget and the nitrate accumulation between S1 and S2, which is the difference of the nitrate loads transported past the two river sections.

In the regulated river reach under study, which is characterized by gravel bottom and colonized by submerged macrophytes, ammonium and nitrite loads were higher upstream and suggested net retention in all seasons, peaking in summer when the primary producers' activity is maximum. Differently, dissolved inorganic carbon and nitrate loads evidenced a significant increase from upstream to downstream in all the investigated seasons. Nitrate and inorganic carbon net export decreased from August to April, with August as the central month for irrigation and April the last month before the start of the irrigation period. From these results, we calculated the annual net export of inorganic carbon and nitrate multiplying the daily values by the number of days between consecutive samplings, and then integrating the results over one year. Despite 6–8 repeated water samplings during the 24 hours, these calculations are based on measurements carried out in single days along different seasons. However, the nitrate concentrations measured in this study are consistent with the seasonal NO3-N concentrations measured by ARPA Lombardy (the authority that manages water monitoring for the WFD) in the period 2009–2017 and by the Laboratory of Aquatic Ecology of the University of Parma in the period 2011–2017 (Fig. C.1 in Supplementary material C).

It was estimated that 2153 ± 174 t DIC y^{-1} and 317 ± 12 t NO3-N y^{-1} were net exported from the 8 km long reach between S1 and S2. These amounts can be explained by element transformation (e.g., respiration or nitrification), and lateral or vertical inputs. As the loads of the other two inorganic N forms were negligible as compared to nitrate, this calculation was done only for the latter. Using dissolved oxygen budgets (not reported in this work) we converted dark river respiration rates (night oxygen uptake along this stretch; from − 1.3 to -5.7 mm O_2 m^{-2} h^{-1} in winter and summer, respectively) into potential nitrification rates (~ 75 t N y^{-1}) according to nitrification stoichiometry. To this purpose, we assumed that 100% of the oxygen consumed was used to oxidize ammonium to nitrate. Results suggest that microbes-mediated processes as nitrification can explain at most 23% of the nitrate accumulation in the river reach in all seasons. Such percentage is a large overestimation of the real value as it was obtained neglecting all other oxygen-consuming processes, including macrophytes, fish, macroinvertebrates, and the whole heterotrophic microbial community respiration. A comparable nitrate production (~ 80 t N y^{-1}) was obtained using the nitrification rate set by Taherisoudejani et al. (2018) in the QUAL2Kw model applied to the Oglio River, a nearby Po River tributary with similar

hydrological characteristics. Pinardi et al. (2014) found that the processes in the hyporheic zone or the microbial metabolism of carbonate dissolution could explain up to 15% of the DIC increase, including the role of macrophytes in modulating dissolved CO_2 saturation values and fixation of C.

If biological processes cannot explain inorganic carbon and nitrate increase, also point pollution sources can be excluded, due to low discharge of small tributaries along this stretch with water chemistry comparable to that of the Mincio River. Another potential source of N and DIC is groundwater, via seasonally variable river-groundwater interactions. Indeed, the level of the phreatic surface increases and interacts with the river due to precipitation, flooding and sprinkler irrigation during the spring-summer period (Racchetti et al. 2019; Severini et al. 2020) (Fig. 7). In a period before and after fertilization (from March to May 2021), Severini et al. (2022) measured in the same area of the Mincio River significantly higher HCO_3^- concentrations in groundwater than in surface water (Appelo and Postma, 2005). Hence, the DIC increase in the investigated river stretch can be associated to the groundwater feeding the Mincio River. Considering the abundant use of organic fertilizers in the area, the higher DIC in groundwater can be related to the presence of calcite ($CaCO_3$) in the mineralogical composition of the aquifer and to the oxidation of the organic matter, which promotes a higher DIC concentration in groundwater. Future investigations should include the mineralogical composition of the aquifer.

5.3. Linking soil N budgets and N riverine export: the key role of the aquifer

The main period of N fertilization is in spring when there is the highest N soil surplus and surface and groundwater pollution risk due to limited crop uptake. The crop harvest occurs mainly in summer and autumn when the N soil budget is in deficit or close to equilibrium, respectively. These data are reflected by an increasing N export by the river reach from spring to summer, favored by large volumes of nitrate-enriched water displaced through the irrigation across the aquifer-river continuum (Isidoro et al. 2006). Using SiO_2 as tracer, Severini et al. (2022) typified the investigated river stretch as a flow-through system, where groundwater feeds the Mincio River in its west bank and it is fed from the river's east bank (Fig. 7). As a result, N-rich groundwater can displace N-poor water from the Mincio River without a significant modification of the river flow (Fig. 7). Our data are consistent with this hydrogeological conceptual model, since the higher NO3-N delta loads were found in summer, when the groundwater level are the highest and there is the maximum groundwater seeping to the Mincio River, highlighting the deep effects of the recharge given by irrigation. On the contrary, some differences were found during the rest of the year, characterized by a less anthropic recharge of the aquifer. These differences are more related to the dissimilar distribution of precipitation and percolation of water and N to groundwater, which fosters the migration of N to the Mincio River. In fact, as we move away from the end of the irrigation period (September), the lower groundwater heads reported in Severini et al. (2022) could result in a lower groundwater seepage to the river (Fig. 7). Having less nutrient enriched water available guarantees a minor nitrate surplus in the river reach, even if N fertilization starts again in winter, resulting in another period with N soil surplus (Figs. 6, 7).

Considering that the mean annual N surplus on the agricultural land in the study area averaged 67 kg ha^{-1} y^{-1}, it is possible to speculate that the agricultural land surface that can potentially generate the NO3-N river export

(317 ± 12 t NO3-N y^{-1}) is equivalent to ~ 4700 ha^{-1}. In addition, dividing this surface by the length of the river reach investigated, it is possible to estimate the width from the river, which is about 2.9 km for each side, that might be involved in the N surplus production. These data allow to speculate that the N surplus was generated in the 25% of the surface of municipalities under study, giving useful information to better address arable land management.

Our results on N input and output trends in agricultural soils and into the river reach at annual and seasonal basis allow to better understand N patterns from land to river and the potential nitrate pollution to surface and groundwater. This information at seasonal resolution can help policy-makers in developing effective plans to improve N management at the macroscale. In fact, this combination of information can guide the identification of proper spatial-temporal management strategies to reduce N pollution and river export to avoid eutrophication processes of water bodies. For example, our results suggest that more nitrate was delivered downstream in summer because of spring soil N excess coupled to flood irrigation over permeable soils. Hence, it is important to focus on agricultural sources (manure and synthetic fertilizers in particular) to better balance N inputs and output by crop harvest (or stock). Our approach was applied in a pilot study at the sub basin level, but it is exportable to the whole basin and to other rivers. It becomes very important to have local information and basin-specific data to perform seasonal analysis on N patterns (Lassaletta et al. 2021).

5.4. Possible remediation strategies in the context of climate change and the regulation of river discharge

Temporal disconnections between N fertilization, transport and uptake in agricultural land can result in low N use efficiency (Robertson and Vitousek, 2009). Specific monitoring of crop growth, nutrient demand and soil availability is useful to obtain a more synchronous nutrient supply in response to crop needs (Quemada et al. 2013). Alternative practices arranged to implement nutrient management directly in the field include actions such as variable rate or split of fertilizer applications matched to crop growth demand, improvements in efficiency of irrigation practices and use of nitrification inhibitors (Lacey and Armstrong 2015; Fernández et al. 2016). The nutrient best management practices, for N, should be designed in view of seasonal N leaching losses and hydrologic export to properly depict crop growth dynamics and N demand, soil conditions and hydrology (Lin et al. 2019).

It is during summer that the investigated reach experienced the highest water nitrate accumulation. An action useful to buffer the N export is the implementation of riparian buffer strips that can promote N retention during the spring-summer irrigation period or the use of cover crops in winter (Dabney et al. 2010; Cole et al. 2020). During winter, our calculations suggest N soil excess in a period where uptake is minimum, and denitrification is likely limited by low temperatures and by the thick unsaturated soil. The latter follows the downward winter migration of the water table, previously discussed. For this reason, the adoption of practices that can favor water retention to increase soil humidity in the cold season and the presence of water in canals, commonly dry in autumn and winter, might be a solution that can favor denitrification process. As an example, the construction of artificial ponds or wetlands can be useful to intercept N runoff from agricultural lands (Nõges et al. 2003; Carstensen et al. 2020).

In the geographical area of our case study, the Alps host a series of large lakes regulated by dams that feed rivers among which the Mincio River. The dams regulate the lake water level and the river discharge with rules

that aims to accumulate water in winter and release it during the irrigation period, adapting also to local meteorology and water inputs to lakes. This regulation practice guarantees sufficient summer level in lakes for tourism and navigation purposes and large water availability for irrigation and electricity production in the downstream river section. Irrigation is supported by several water abstraction infrastructures that facilitated agriculture and animal farming activities. Irrigation practices, supported mainly by flooding irrigation in the sector of the Po River plain including our study area are carried out over permeable soils, and favor the recharge of the aquifer mainly in summer (Rotiroti et al. 2019). Therefore, water retention upstream during non-irrigation periods and flood irrigation with large water volumes during summer are probably the main drivers of the groundwater head variation, which is subject to strong seasonal differences (Taherisoudejani et al. 2018). Under the current climate change scenario, also in this geographical area, the rapid changes of global warming are manifested with lower precipitation, dry winters, heatwaves and storms events, and an increasing number of consecutive days with high temperatures (Cifrodelli et al. 2015; Pedro-Monzonís et al. 2016; Lassaletta et al. 2021; Ranasinghe et al. 2021). The response to these global trends could increase or decrease river nitrate concentration depending on regional or site-specific linkage between N concentration and discharge (Stelzer et al. 2020). For this reason, the geographical sector under study seems extremely vulnerable to climate change as the system is depicted and managed for large water availability (i.e., large lakes regulation, high water demanding crops, and flooding as main irrigation practice) and therefore a discussion on water management at political level is urgent. Predicting scenarios on the fate of the N excess with different water availability is difficult, we can hypothesize a reduction of water discharge from rivers and consequently from irrigation that will not recharge sufficiently the groundwater due to its deep level (Taherisoudejani et al. 2018). This condition will lead to more thick vadose zones, fostering a higher nitrification rate and nitrate accumulation in soil during winter, whereas denitrification, the main process that removes N permanently from the system, is favored in water saturated soils with high organic matter (Ascott et al. 2017). In soil and rivers close to N saturation, it is expected a lower nitrate retention efficiency and therefore an increase in N availability and vertical and horizontal transfer (Stelzer et al. 2020). Moreover, for the future it can be expected a delay in the river feeding by groundwater with hot-moments of N mass transfer. In fact, we can expect that with the increment of unsaturated zone, the rate of soil denitrification will be reduced and conversely the nitrification process will be favored supplying a short N mass-transfer as soon as the first rainfall or flooding irrigation will occur, carrying water with high N concentration to surface or groundwater. A possible solution to limit this hot-moment can be the improvement of irrigation practices with less water consumption and a more widespread use of precision farming supported for example with remote sensing technique (Nutini et al. 2021). Such a new vision on the irrigation practices can allow a lower winter water retention in the Lake Garda, that can be partially used in the non-irrigation period to guarantee a minimal vital flow in a certain number of drainage canals as well as in the Mincio River favoring denitrification process also in autumn and winter, although with lower rates driven by lower temperatures.

6. Conclusions

Published soil system budgets in agricultural areas generally reveal net N excess on an annual basis, whereas the present study reveals seasonally variable inventories of inputs and outputs, resulting in periods of large N excess and periods of pronounced deficit. The export of N excess via the river draining the investigated area has a temporal lag that depends on irrigation, vertical migration of the water table and subsurface water flow.

Flood irrigation first fills the unsaturated zone and then favors river-groundwater interactions. Subsurface water flow replaces N-poor river water with N-rich groundwater. Seasonal soil N budget and the mechanisms of N transfer described in this study should foster more efficient agricultural practices, minimizing N losses and improving N use. Results from this work should also be carefully considered in future planning of agricultural and irrigation activities, in a scenario of climate change and variable availability of water. Winter retention of water in lakes, upstream the agricultural areas, has serious drawbacks as it will increase the volume of the unsaturated soil and the production of nitrate via organic N ammonification and nitrification. Adaptive strategies based on precision farming, new material to retain soil humidity, irrigation techniques alternative to flooding and a management of the canal network targeting the restoration of biogeochemical services (e.g., N-uptake and denitrification) seem effective and sustainable options.

Declarations

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Figures

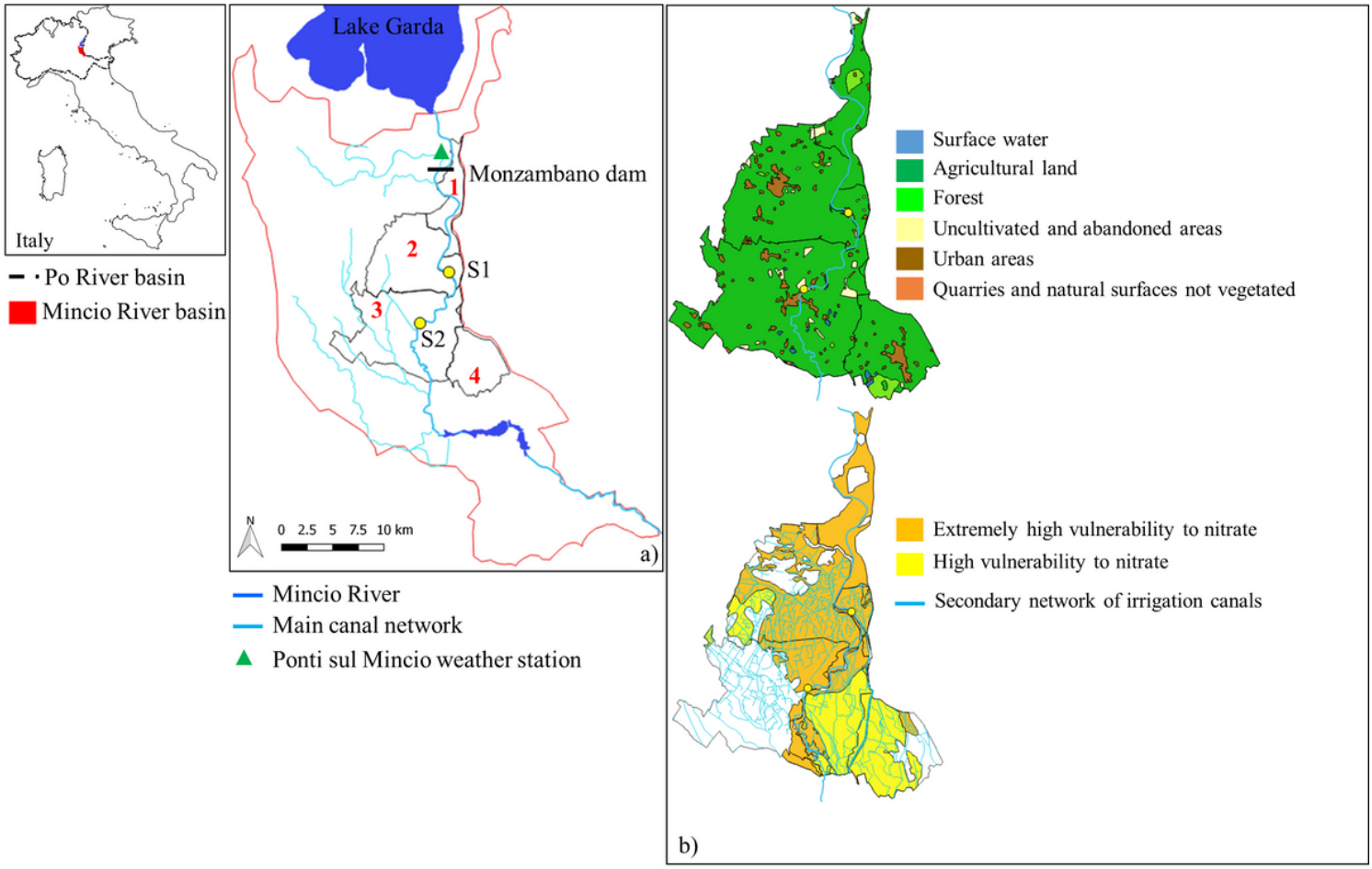

Figure 1

Maps of the study area: the Mincio River segment from Pozzolo dam (S1) to Goito village (S2) (yellow points = water sampling stations). a) Municipalities where the nitrogen mass budget was performed are reported (1 - Valeggio sul Mincio, 2 - Volta Mantovana, 3 – Goito, 4 - Marmirolo). b) Land use and maps of soil vulnerability to nitrate are reported for the four municipalities under study.

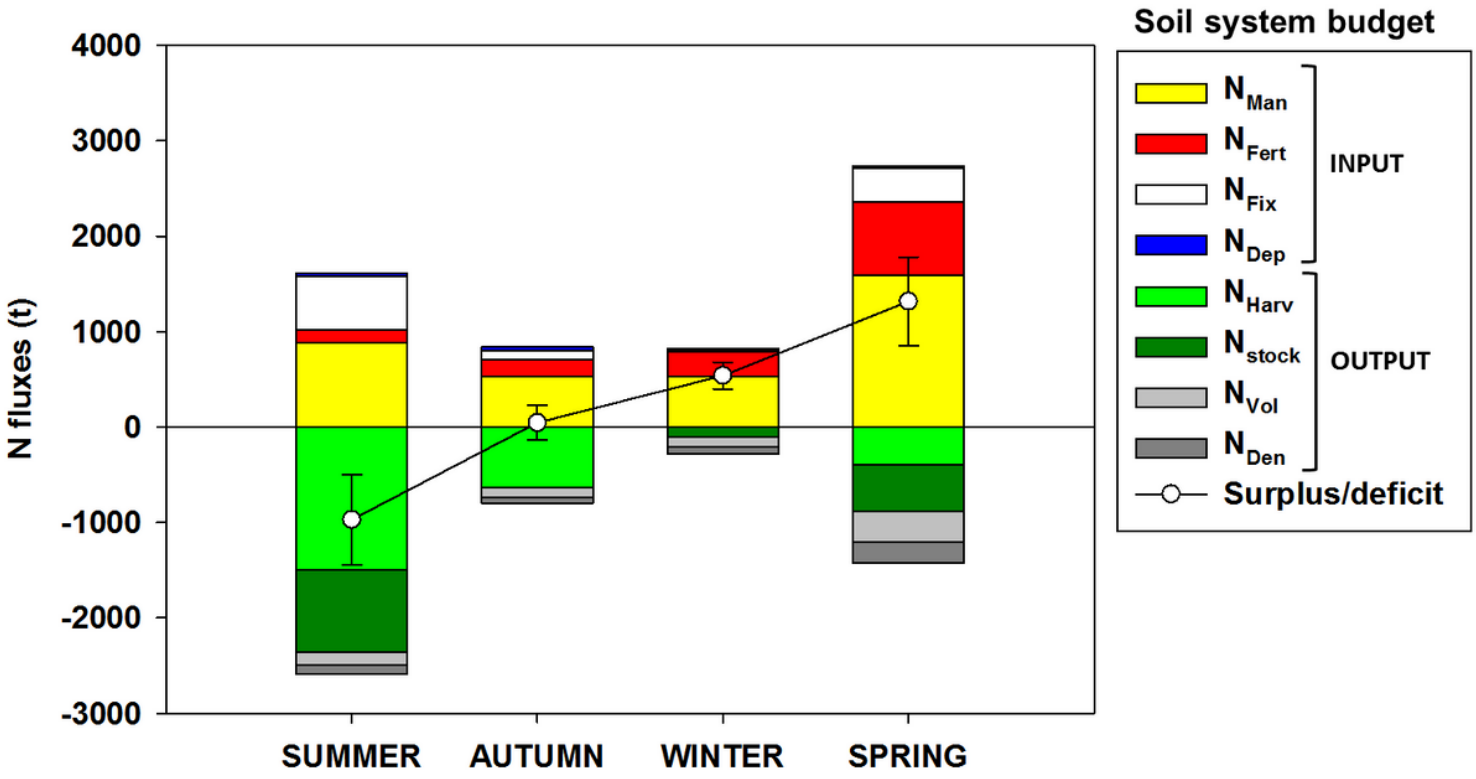

Figure 2

Components of the Soil System Budget (SSB) of nitrogen (N) for the study area within the Mincio River watershed for all seasons. N_{Man} = N in livestock manure applied to agricultural soils; N_{Fert} = N in synthetic fertilizer applied to agricultural soils; N_{Fix} = agricultural N_2 fixation associated with N fixing crops; N_{Dep} = atmospheric N deposition on agricultural land; N_{Harv} = N exported from agricultural soils with crop harvest; N_{stock} = organic N in crop's standing stock; N_{Vol} = NH_3 volatilization in agricultural soils; N_{Den} = denitrification in agricultural soils. White dots represent seasonal N budgets (Σ INPUTS - Σ OUTPUTS); positive values suggest surplus whereas negative values suggest deficit.

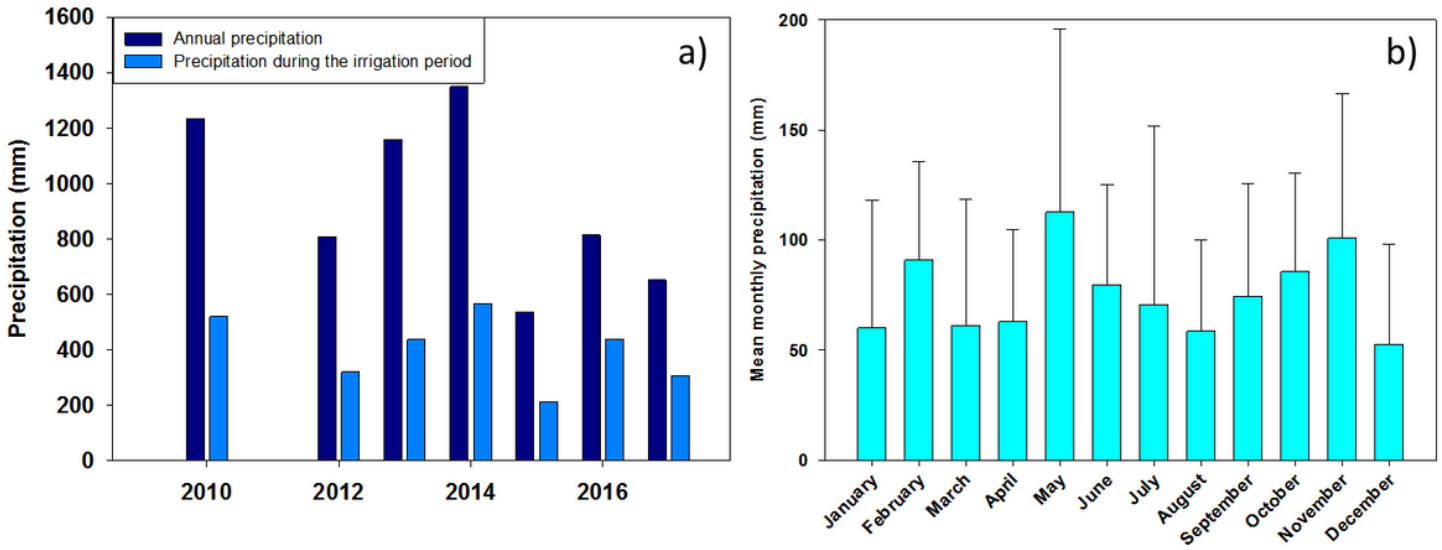

Figure 3

Annual precipitation and the fraction of precipitation during the irrigation period (from May to September) (a) and mean monthly precipitation (± standard deviation) (b) in the period from 2010 to 2017 at Ponti sul Mincio meteorological station (see Fig. 1 for the localization) (2011 was not considered due to missing data for August and September).

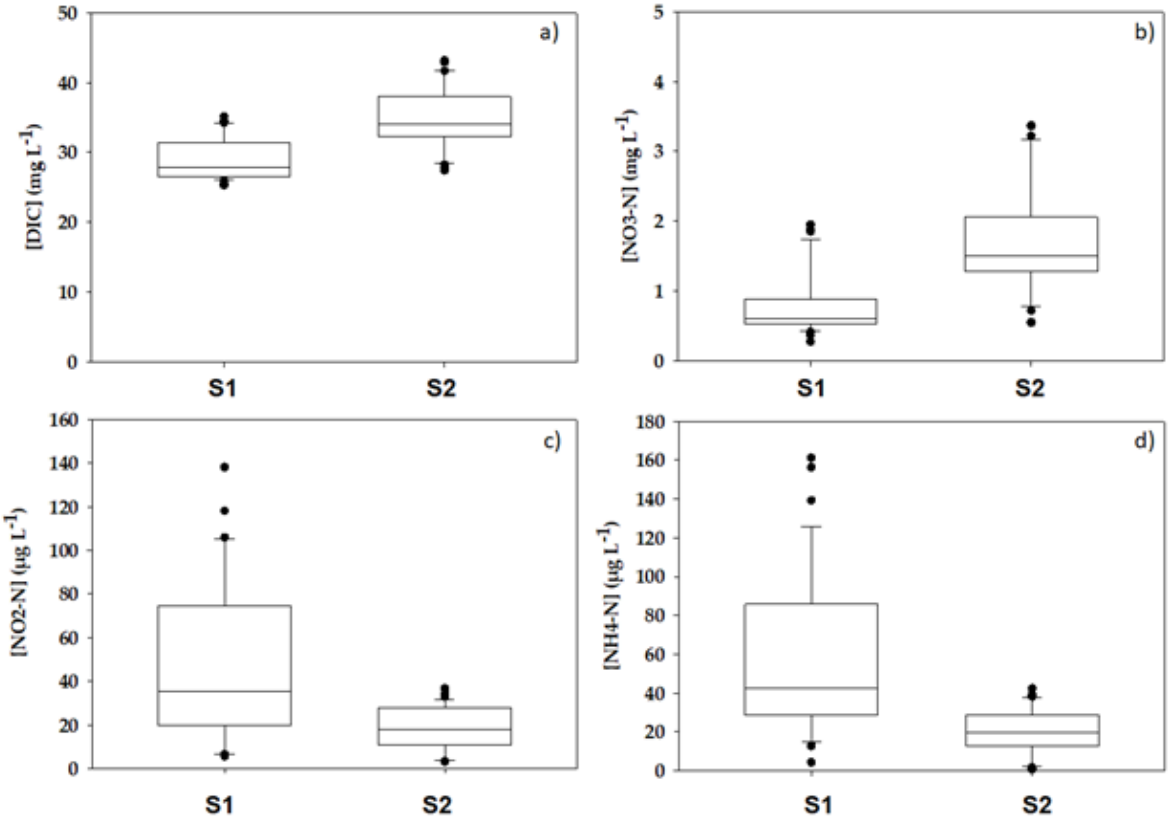

Figure 4

Box plot showing the concentrations of dissolved inorganic carbon (DIC; a), and of nitric (NO3-N; b), nitrous (NO2-N; c) and ammonium (NH4-N; d) nitrogen measured seasonally from August 2016 to June 2017 at S1 and S2. Note different concentration units.

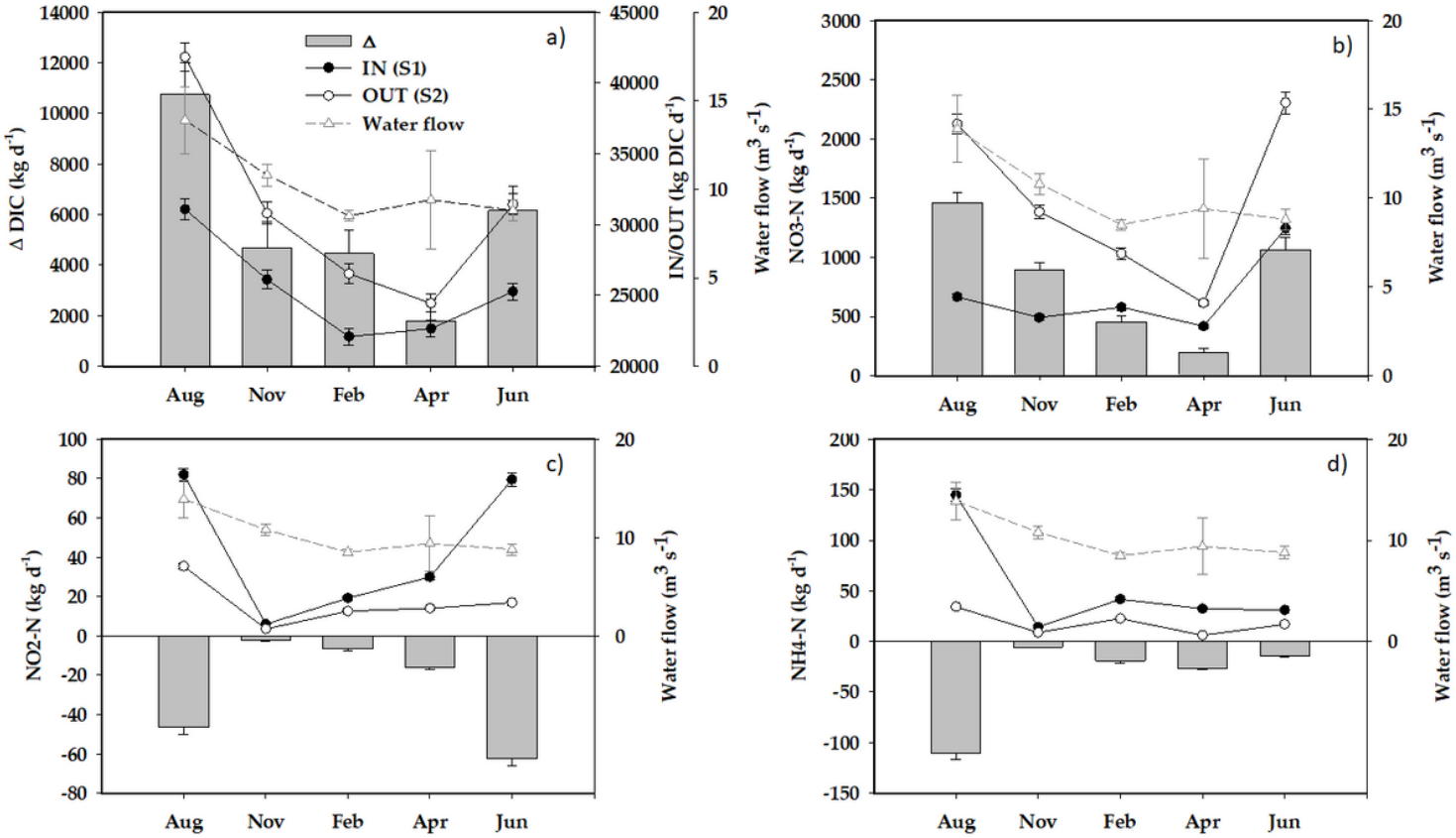

Figure 5

Daily loads of inorganic carbon (DIC; a), nitric nitrogen (NO3-N; b), nitrous nitrogen (NO2-N; c), and ammonium nitrogen (NH4-N; d) transported at the extremes of the studied river reach and their differences (Δ=S2-S1) in the period August 2016 to June 2017. Water flow is also reported. Mean values are given, with error bars corresponding to ±1 standard deviation.

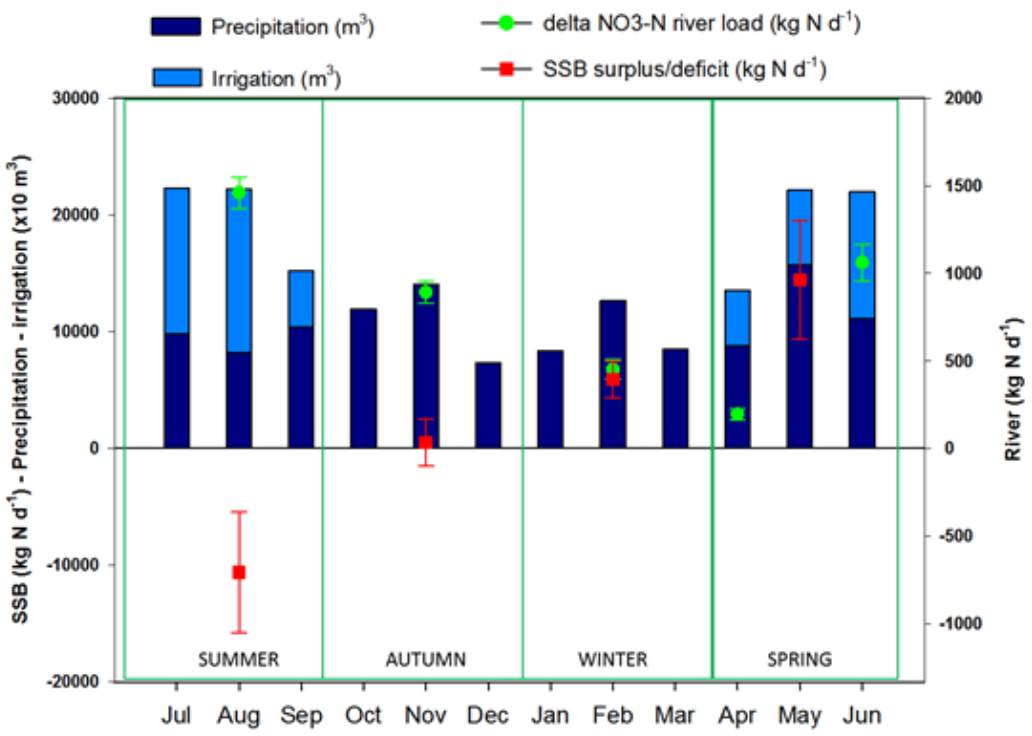

Figure 6

Histograms report monthly water input due to precipitation and irrigation in the municipalities of the Mincio basin under study. Green dots show the delta nitrate loads of the river reach (delta NO3-N river load) in the five sampling dates and red squares show seasonal N budget of agricultural soils (SSB – Soil system budget – surplus/deficit).

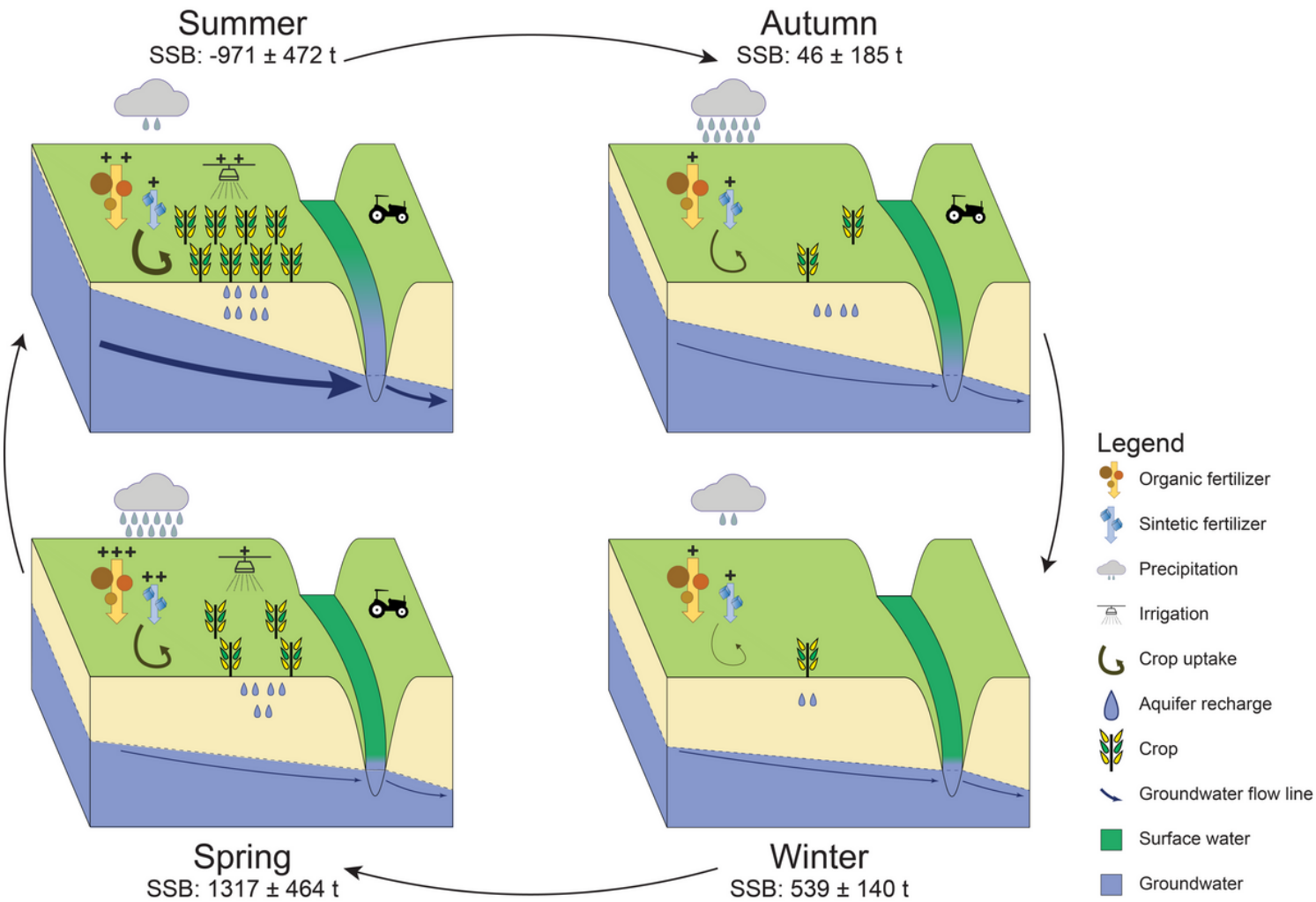

Figure 7

Synthesis of the seasonal nitrogen budgets at agricultural land and at river section. The relation with the groundwater is also reported. SSB = Soil System Budget.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplMaterA.docx
- SupplMaterB.docx
- SupplMaterC.docx