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Soil system budgets of N, Si and P in an agricultural irrigated watershed: surplus, differential export and underlying mechanisms

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Abstract Ongoing socio-economic and climatic changes can differentially affect the biogeochemistry of the key nutrients nitrogen (N), silica (Si), and phosphorus (P) by altering their soil budgets, their transfer to aquatic environments and their ecological stoichiometry. This may lead to cascade consequences for aquatic communities and biogeochemical processes. Soil budgets, river export, and N, Si, and P ecological stoichiometry were assessed in a heavy impacted basin (Mincio River, Italy) in two decades (1991–2000; 2001–2010). The main aim was to analyse element-specific mechanisms of terrestrial-aquatic transport and retention within aquatic habitats. Budget results suggest a net accumulation (inputs exceeding outputs) of all nutrients in agricultural lands, mainly due to livestock manure, with a reduction for N (196 kg N ha^{-1} year^{-1} in 2000, and 132 kg N ha^{-1} year^{-1} in 2010), and constant values for Si (up to 3 kg Si ha^{-1} year^{-1}) and P (43 kg P ha^{-1} year^{-1}) along the study period. River export of N and P accounted for 3–27% and $\sim$ 2% of N and P soil net accumulation, respectively, while Si export was significantly greater (25 kg Si ha^{-1} year^{-1}) than Si net accumulation on farmlands. The stoichiometry of net nutrient accumulation in soils was not reflected by the stoichiometry of nutrient riverine export, due to

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element-specific mechanisms. We speculate that N and Si vertical and horizontal mobilization is increased by the irrigation loop, while P retention is favored by limited erosion due to limited slopes in the Mincio River basin. The simultaneous analysis of N, Si and P allows us to better understand the different paths, transformation and retention mechanisms at the watershed scale.

Keywords N budget · P budget · Si budget · Nutrient retention · Stoichiometry · Watershed

Introduction

In the last decades, the impact of human activities on the biogeochemical cycles of nitrogen (N), phosphorus (P) and silica (Si) has increased in scale (Bernot and Dodds 2005; Muhlolland et al. 2008; Paerl 2009; Han and Allan 2012). Inland and coastal waters have become more and more enriched with N and P due to intensive soil fertilization from agriculture and wastewater discharge (Galloway et al. 2008; Paerl 2009). Nutrient excess can favour and accelerate eutrophication processes up to levels where algal growth cannot be controlled by pelagic or benthic grazing, resulting in biomass accumulation, organic enrichment and oxygen depletion (Carpenter et al. 1998; Rabalais et al. 2002). The simultaneous reduction of Si delivery to aquatic ecosystems has resulted in unbalanced nutrient stoichiometry, favouring harmful algal blooms and further impacting the functioning of benthic and pelagic compartments (Billen and Garnier 2007; Howarth et al. 2011; Bresciani et al. 2014, 2017; Vybernaite-Lubiene et al. 2017).

Global changes of biogeochemical cycles have also altered the scale of analysis (Lehner et al. 2006; Galloway et al. 2008). Research in the field of eutrophication and aquatic biogeochemistry, traditionally targeting single water bodies or single nutrients, now tends to couple aquatic ecosystems to their watersheds or to macroregions and consider simultaneously the dynamics of different elements (Chapin et al. 2002; Galloway and Cowling 2002; Viaroli et al. 2015; HELCOM 2015). Climatic anomalies and anthropogenic pressures in catchments as agriculture, urbanization, landscape simplification, and river damming may in fact produce a wide range of contrasting element-specific effects, either amplifying or reducing their delivery or retention and resulting in strong impact on their ecological stoichiometry (Bennett et al. 2001; Sternberg 2006; Gruber and Galloway 2008; Romero et al. 2016). Few studies have simultaneously analysed long-term changes of N, Si and P loads, despite the well-recognized role of their relative abundance on algal community composition (Billen et al. 2001; Romero et al. 2013). Silica genesis and export from watersheds is generally calculated from the lithology and assumed to vary mostly due to hydrological features (Billen et al. 2001; Garnier et al. 2002). The recent literature focusing on the terrestrial Si cycle stresses how agricultural activities may impact the delivery of this element to the coastal areas and should therefore be considered when analysing budgets with respect to long-term variations of land use (Carey and Fulweiler 2012).

The percentage of net N load generated within a watershed which is not exported via river discharge ranges on average between 40 and 95%, with a substantial variability observed between temperate and arid regions (Howarth et al. 2006; Schaefer et al. 2009; Lassaletta et al. 2012; Romero et al. 2016; Goyette et al. 2016). Retention includes processes as incorporation in sediments through primary production uptake or loss to the atmosphere via denitrification or anammox (Burgin and Hamilton 2007; Zhou et al. 2014; Shen et al. 2016). Similar or even higher percentages (85–99%) are reported for P retention (Han et al. 2011; Hong et al. 2012; Zhang et al. 2015) which might be coupled to those of Si via diatoms blooms and nutrient uptake (Le et al. 2010; Chen et al. 2014a). Studies focusing on Si are scarce as compared to those on N and P and global estimates of Si retention are affected by a large degree of uncertainty (Turner et al. 2003; Beusen et al. 2009; Seitzinger et al. 2010).

Several processes explain how N is retained within watersheds through uptake by crops and natural vegetation, storage in soils, percolation and accumulation in groundwater (Bartoli et al. 2012; Billen et al. 2013; Soana et al. 2017; Ascott et al. 2017). Microbially-mediated N transformations, including denitrification, anammox and N-fixation, are extensively studied in terrestrial and aquatic environments, while methodological difficulties arise for groundwater (Groffman et al. 2006; Baron et al. 2013; Castaldelli et al. 2015). The limited dataset of some soil-related processes limits our knowledge of how they are regulated or affected by climatic anomalies (i.e. drought or precipitation extremes), or agricultural practices (i.e. irrigation or land use) (Vagstad et al. 2004).

The increasing P accumulation in agricultural soils elevates the potential P erosion, runoff and percolation to surface and groundwater (Bennett et al. 2001; Prasuhn and Sieber 2005). Dissolved P losses can be significant in soils where iron (Fe), aluminum (Al), and calcium (Ca) absorption capacity is saturated, allowing P to move more readily toward aquatic ecosystems (Sims et al. 1998). Riparian buffers and wetland areas, impoundments, and conservation agriculture practices may trap some of the exported P, while the rest may contribute to eutrophication processes, and be retained via assimilation or incorporation within sediments (Bennett et al. 2001; Wang and Li 2010; Canga et al. 2016; Kronvang et al. 2016).

Silica delivery to aquatic ecosystems is assumed to be regulated by processes as chemical weathering of silicate minerals in rocks and soils (Sommer et al. 2006; Struyf et al. 2009). However, anthropogenic pressures such as hydrological alterations (Ittekkot et al. 2000; Frings et al. 2014) and the agricultural production loop (Vandevenne et al. 2011; Viaroli et al. 2013) can affect the biogeochemical Si cycle. Among hydrological alterations, river damming has intensified during the last century, favouring diatom growth and settling of their frustules in reservoirs, resulting in net upstream retention and less export of particulate Si to the coastal zone (Harrison et al. 2012; Maavara et al. 2014). Concerning the agricultural production loop, crops harvest results in a significant export of biogenic silica (BSi) from soil, which can cause a progressive depletion of bio-available silica due to intensive agricultural practices (Vandevenne et al. 2011, 2015; Carey and Fulweiler 2012, 2015). Manure spreading and burial of crop residues can increase BSi in soils, but these contributions remain understudied (Viaroli et al. 2015). For example, a very few data on livestock waste Si content are available (Song et al. 2014; Tsai and Liu 2015).

Under a scenario of increased human and climatic perturbations, the understanding of the factors controlling N, Si and P export from watersheds to aquatic environments is becoming crucial. Perturbations may in fact differentially affect the three elements cycling and alter their ecological stoichiometry, which regulates the composition of algal communities. Significant shifts from molar ratios as that of Redfield (C:Si:N:P = 106:15:16:1; Brzezinski 1985) may produce large changes in algal communities. Silica limitation for example favours the bloom of non-siliceous algae as cyanobacteria or dinoflagellates (Billen and Garnier 2007; Bresciani et al. 2014, 2017; Vybernaite-Lubiene et al. 2017). The increasing scale of anthropogenic impacts on aquatic ecosystems fosters to increase the spatial scale of process analysis (e.g. from rivers to their watersheds). It also advocates the need for a multi-element approach with the ecological stoichiometry theory as conceptual reference.

In this study we calculated the N, Si and P soil budgets in 2000 and 2010, analysed in-stream loads of these nutrients in two decades (1991–2000; 2001–2010), and their stoichiometry in an agricultural basin (Mincio River, Northern Italy). Our main goal was to discuss the net export of N, Si and P from a human impacted basin by coupling the terrestrial and aquatic compartments. We matched watershed budgets with in-stream transport of N, Si and P and we analysed discrepancies among surplus or deficit (a nutrient input that exceeds outputs, or viceversa) at the basin scale and effective export from the watershed. We discuss such discrepancies with respect to natural and artificial catchment features (i.e. presence of large wetland areas, dense irrigation network, discharge regulation by dams, permeable and vulnerable soils) and with respect to ecological stoichiometry and eutrophication. The analysed basin lays within the Po River watershed, the most densely populated and heavily exploited area of Italy for agriculture and animal farming. The coupled analysis of terrestrial and aquatic ecosystems seems particularly interesting in irrigated basins as the Mincio. Here, the capillary network of artificial canals and the flooding-based irrigation causes a fast vertical and horizontal transfer of solutes. Therefore, any changes in land use or agricultural practices can produce an effect on water chemistry and be detected with a very short time lag (Balderacchi et al. 2016).

We hypothesized: (i) high N surplus in agricultural lands, easily mobilized into surficial and groundwater due to irrigation over permeable soils (Racchetti et al. 2011; Soana et al. 2017); (ii) high P loads but little P export, due to effective retention in soils, reservoirs, and wetlands (Canga et al. 2016; Kronvang et al. 2016); (iii) Si retention within watersheds and little export, due to discharge regulation (Viaroli et al. 2013); (iv) unbalanced ecological stoichiometry in aquatic ecosystems due to a generalized N excess and Si and P limitation. In-stream N, Si and P loads and their ecological stoichiometry were assessed with respect to: (a) their budgets in agricultural soils and their temporal variation in the last decade; (b) irrigation practices, as driver of their transport from terrestrial to aquatic ecosystems, and (c) internal processes (i.e. nutrient dynamics in both the canal network and main river course, including sedimentation, denitrification and primary producer uptake).

Materials and methods

Study area

The Mincio River (watershed area 855 km^2, average annual natural discharge 60 m^3 s^{-1}) originates from the Lake Garda and after 75 km flows into the Po River (Northern Italy) (Fig. 1). The Mincio watershed is characterized by Cambisols and Calcisols soils (European Commission 2005). The high-medium and the low plain are characterized by calcareous gravel or silty-clay deposits, respectively, which generate fertile soils, exploited by intensive agriculture (Utilized Agricultural Area - UAA covers $\sim$ 70% of the total watershed) and livestock farming (136 $\times$ 10^3 cattle and 483 $\times$ 10^3 swines). Manure and chemical fertilizers are used to improve crop production, but at the same time increase the risk of N pollution in the vulnerable soils of the basin (Lombardy Region 2006). Maize is the main crop cultivated in the Mincio watershed (30%), followed by feed crops (27%), wheat (11%), and permanent grasslands (9%) (National Institute of Statistics 2010a). The hydrological regime of the river is regulated upstream by the Monzambano dam, and downstream by a series of weirs or dams which feed a capillary network of artificial canals for irrigation and industrial purposes and to buffer discharge variations, to avoid flooding and risk for the large number of villages (and the town of Mantua) located along the course. The flow variations are mainly influenced by agricultural activities, for example in the irrigation period (from late April to early September) the average water discharge from Lake Garda is 74 m^3 s^{-1}, while in the rest of the year is about 26 (or at minimum 16) m^3 s^{-1} (Lombardy Region 2006).

In this irrigated system the linear development of artificial canals sums nearly 2000 km, and develops all over the territory. In the Mincio River basin the urbanized land is $\sim$ 10% of the watershed area and the human population is $\sim$ 207,000, resulting in an average density of 242 inhabitants km^{-2} (2011). The river receives sewage from two large wastewater treatment plants (WWTP) with 330,000 population equivalent (p.e.) (collecting wastewater produced upstream, from the Garda Lake municipalities) and 170,000 p.e. (from Mantua town, within the watershed), respectively. The Mantua Lakes and the wetlands (Valli del Mincio and Vallazza) with a total surface of $\sim$ 23 km^2 were created from a meander of the Mincio River which was dammed in the twelfth century. The Mantua Lakes are shallow eutrophic fluvial lakes characterized by low water renewal time, rapid infilling, high nutrient and organic matter loads, and by the coexistence of algal and macrophyte communities (Pinardi et al. 2011, 2015; Bresciani et al. 2013, 2017; Bolpagni et al. 2014; Villa et al. 2017).

Mincio basin features

Annual precipitation in the Mincio watershed is rather uniform along the historical dataset and from upstream to downstream stations (mean $\pm$ standard deviation of the period 2005–2010: 891 $\pm$ 220 mm year^{-1} in Monzambano, 742 $\pm$ 226 mm year^{-1} in Goito, and 706 $\pm$ 304 mm year^{-1} in Mantua) (data sources: CO.DI.MA. 2017; ARPA Lombardy 2017). The precipitation during the April-September irrigation period is not significantly different between high, medium and low plain, and provides $\sim$ 50% of the total annual. Surface waters are the main sources of irrigation (total volume 183 $\times$ 10^6 m^3 year^{-1} in 2010), in particular from aqueduct or irrigation consortium with delivery service on request or in turn (Fig. 1 in Online Resource 1) (National Institute of Statistics 2010a). During 2010, the irrigated surface was $\sim$ 500 km^2, close to 66% of the whole catchment. The main irrigation systems are flooding and sprinkler irrigation, in terms of both volume (40% and 55% of total water use, respectively) and irrigated surface (34% and 60% of the total, respectively) (Fig. 2 in Online Resource 1). Irrigation by flooding is

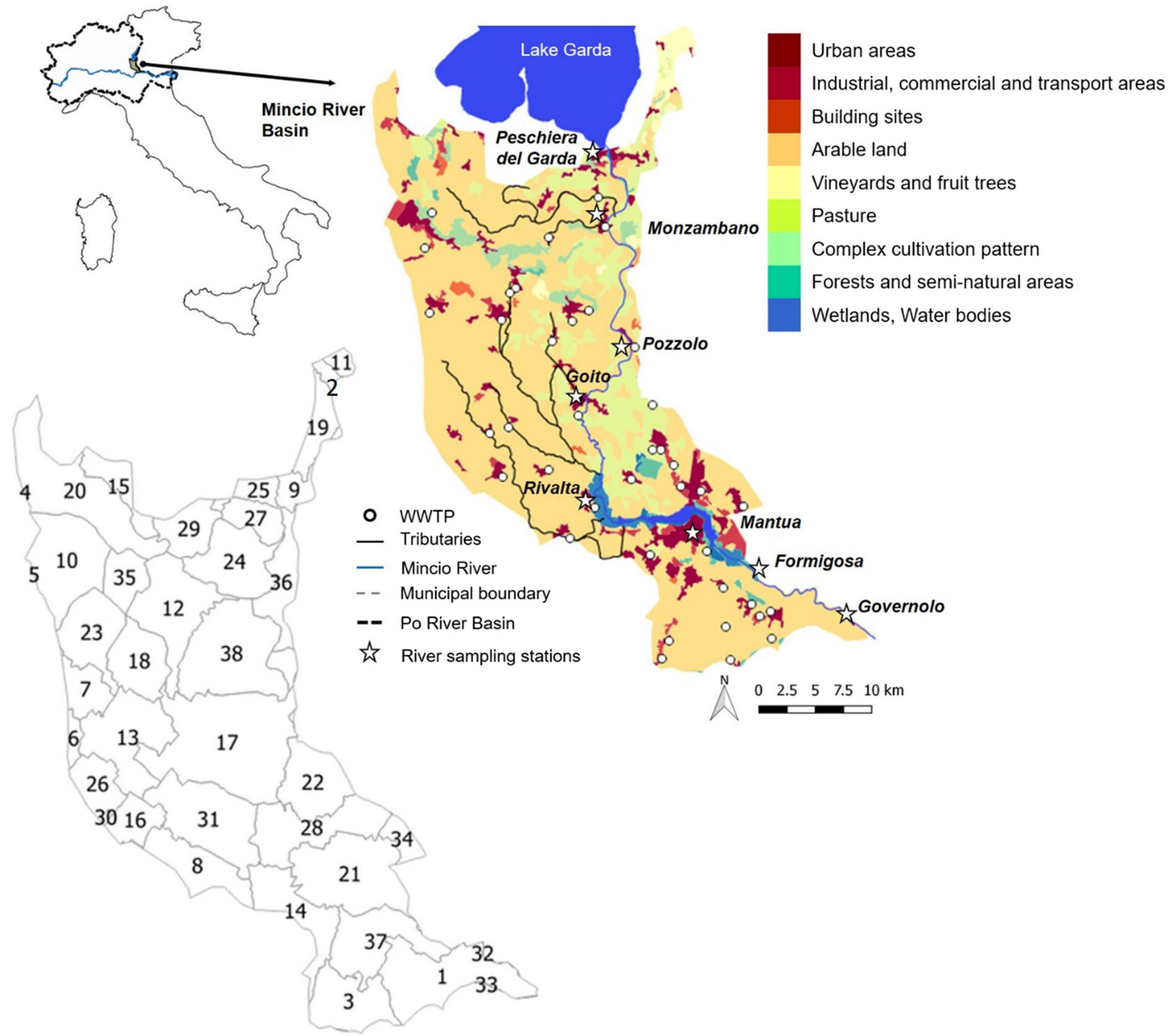

Fig. 1 Land use (right) and municipalities (left) maps of the Mincio River basin (source: Corine Land Cover 2012) and its location within the Po River basin (Italy). Tributaries, wastewater treatment plants (WWTPs), and sampling stations along the Mincio River are also reported. (*1* Bagnolo San Vito, *2* Bardolino, *3* Borgoforte, *4* Calcinato, *5* Carpenedolo, *6* Casaloldo, *7* Castel Goffredo, *8* Castellucchio, *9* Castelnuovo del Garda, *10* Castiglione delle Stiviere, *11* Cavaion Veronese, *12* Cavriana, *13* Ceresara, *14* Curtatone, *15* Desenzano del Garda, *16* Gazoldo degli Ippoliti, *17* Goito, *18* Guidizzolo, *19* Lazise, *20* Lonato, *21* Mantova, *22* Marmirolo, *23* Medole, *24* Monzambano, *25* Peschiera del Garda, *26* Piubega, *27* Ponti sul Mincio, *28* Porto Mantovano, *29* Pozzolengo, *30* Redondesco, *31* Rodigo, *32* Roncoferraro, *33* San Benedetto Po, *34* San Giorgio di Mantova, *35* Solferino, *36* Valeggio sul Mincio, *37* Virgilio, *38* Volta Mantovana). (Color figure online)

mainly applied in the municipalities of the high-medium plain where soils are permeable and vulnerable to nitrate (Fig. 2a in Online Resource 1). Sprinkler irrigation with delivery service on demand is the most used irrigation system in the low plain, where soils are less permeable, and in the municipalities where the main cultivations are fruits and vegetables (Figs. 1 and 2b in Online Resource 1). Annual water volumes used for irrigation by flooding are in the range 1242–6863 m^3 ha^{-1} $year^{-1}$ (median 4229 m^3 ha^{-1} $year^{-1}$), whereas those used for sprinkler irrigation are in the range 731–3868 m^3 ha^{-1} $year^{-1}$ (median 3185 m^3 ha^{-1}) (Fig. 2c and d in Online Resource 1). The municipalities located in the medium plain use the highest volume of water per hectare of surface to irrigate crops (Fig. 2c in Online Resource

1). Soil texture of the Mincio basin is mainly gravel and sand (Fig. 1 in Online Resource 1) and the high and medium plain are characterized by high and extremely high vulnerability to nitrate leaching (Fig. 2 in Online Resource 1) (data source: shape-file provided by the Province of Mantua).

N, Si and P soil budgets calculation

Nitrogen, Si and P balances in agricultural soils were compiled for the years 2000 and 2010, which refer to available census data for the periods 1991–2000 and 2001–2010, respectively. Census data were integrated in a nutrient budgeting approach proposed by Oenema et al. (2003) and adapted and previously applied to the Po River system and some of its sub-basins (Soana et al. 2011; Castaldelli et al. 2013; Viaroli et al. 2018) and other Italian temporary rivers (De Girolamo et al. 2017). Soil nutrient budgets were determined by comparing N, Si and P inputs and outputs across the productive agricultural surface within the Mincio basin. The sum of inputs and outputs results in a net which is a proxy of equilibrium, surplus or deficit and which is directly linked to riverine export (Fig. 2). Soil system budgets (SSBs) were calculated as follow:

$$\mathrm{SSB\ N} = \mathrm{N_{Man}} + \mathrm{N_{Fert}} + \mathrm{N_{Fix}} + \mathrm{N_{Dep}} - \mathrm{N_{Harv}} - \mathrm{N_{Vol}} - \mathrm{N_{Den}} \quad (1)$$

$$\mathrm{SSB\ Si} = \mathrm{Si_{Man}} + \mathrm{Si_{Dep}} - \mathrm{Si_{Harv}} \quad (2)$$

$$\mathrm{SSB\ P} = \mathrm{P_{Man}} + \mathrm{P_{Fert}} + \mathrm{P_{Dep}} - \mathrm{P_{Harv}} \quad (3)$$

where N_{Man}, Si_{Man}, P_{Man} = N, Si, and P in livestock manure applied to agricultural soils; N_{Fert} and P_{Fert} = synthetic N and P fertilizer applied to agricultural soils; N_{Fix} = agricultural N_2 fixation associated with N fixing crops; N_{Dep}, Si_{Dep}, P_{Dep} = atmospheric N, Si and P deposition on agricultural land; N_{Harv}, Si_{Harv}, P_{Harv} = N, Si and P exported from agricultural soils with crop harvest; N_{Vol} = NH_3 volatilization in agricultural soils; N_{Den} = denitrification in agricultural soils.

Nutrient budgets were first calculated for each of the 38 municipalities totally or partially included in the catchment boundaries, then aggregated to the basin scale within a GIS (QGIS software 2.18). Balance computations were based on simple equations that convert farming census data into N, Si and P equivalents. The approach relies on high spatial resolution datasets and site-specific agronomic coefficients (Table 1). Where it was possible, N, Si and P balance terms were calculated by means of data gathered from the study area. Where such data were not available, coefficients taken from the literature were used to complete the budgets. Input, output, and surplus or deficit in each municipality as well as the overall nutrient balance at the watershed level were

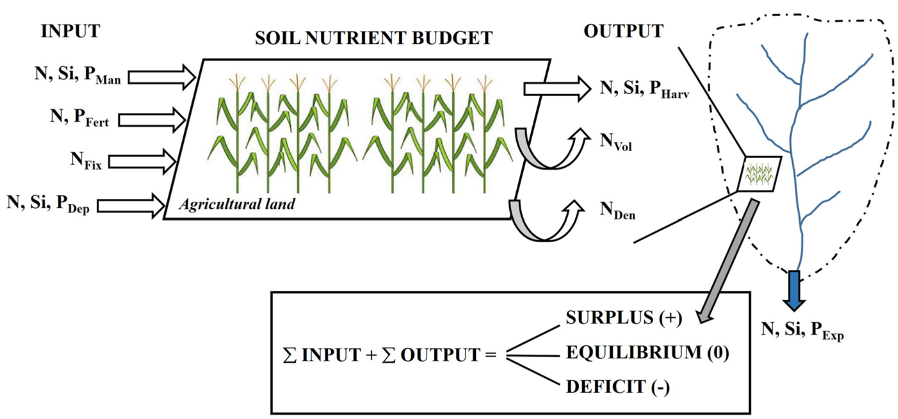

Fig. 2 Diagram of major components of the Soil System Budget (SSB) calculated for nitrogen (N), silica (Si), and phosphorus (P) in a river watershed. SSB is defined as the difference between nutrients input and output summation. Input terms are: livestock manure (N, Si, P_{Man}) and synthetic fertilizer (N, P_{Fert}) applied to agricultural soils; agricultural N_2 fixation (N_{Fix}) associated with N fixing crops; and atmospheric deposition (N, Si, P_{Dep}) on agricultural land. Output terms are: export from agricultural soils with crop harvest (N, Si, P_{Harv}); NH_3 volatilization in agricultural soils (N_{Vol}); and denitrification in agricultural soils (N_{Den}). Nutrients are either subject to watershed retention processes or riverine export (N, Si, P_{Exp})

Table 1 Sources of statistical data and coefficients used in the calculations of N, Si, P budget in agricultural soils

Budget item	Data type (spatial resolution)	Sources
Livestock manure	Livestock density (municipality level)	5th and 6th General Census of Agriculture, National Institute of Statistics (2000a, b, 2010a)
	Animal live weights	DM (07/04/2006), ISTAT (2006), Crovetto and Sandrucci (2010), Song et al. (2014), Pratt et al. (2015) and Tsai and Liu (2015)
	Manure production coefficients	
	N and P excretion rates	
	Si content in manure	
Synthetic fertilizers	Synthetic fertilizer distribution (province level)	Agriculture and livestock data, National Institute of Statistics (2000a, b, 2010b)
	N and P content	Agriculture and livestock data, National Institute of Statistics (2000a, b, 2010b) and Vitosh (1996)
	Utilized agricultural area by land use (municipality level)	5th and 6th General Census of Agriculture, National Institute of Statistics (2000a, b, 2010a)
Biological N fixation	Utilized agricultural area by land use (municipality level)	5th and 6th General Census of Agriculture, National Institute of Statistics (2000a, b, 2010a)
	Crop annual yield (province level)	Agriculture and livestock data, National Institute of Statistics (2000a, b, 2010b)
	Crop N content, N in crop residues	Rural Development Program for 2007–2013, Lombardy Region;
		Water Protection Plan, Lombardy Region (2006)
Atmospheric deposition	N deposition	National maps of oxidized N compounds deposition (EMEP-Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe 2017) http://www.emep.int
	P deposition	Mosello et al. (2002), Guieu et al. (2010) and de Fommervault et al. (2015)
	Si deposition	Giacomelli et al. (1999)
Crop harvest	Utilized agricultural area by land use (municipality level)	5th and 6th General Census of Agriculture, National Institute of Statistics (2000a, b, 2010a)
	Crop annual yield* (province level)	Agriculture and livestock data, National Institute of Statistics (2000a, b, 2010b)
	N and P elemental composition	Rural Development Program for 2007–2013, Lombardy Region
	Si elemental composition	Pennington (1991), Hodson et al. (2005), Powell et al. (2005), Sferratore et al. (2006), Vandevenne et al. (2011) and Viaroli et al. (2013)
Ammonia volatilization	Percentage loss of the supplied N	Minoli et al. (2015) and Pan et al. (2016)
Denitrification in soils	Percentage loss of the supplied N	Castaldelli et al. (2013)

*Crop yields are calculated from the yearly production and the corresponding cultivated area

expressed in unit of mass per time (t N year^{-1}, t Si year^{-1}, t P year^{-1}). Calculation of nutrient input and output terms are described in detail in text and tables reported in Online Resource 2. In addition, we calculated N, Si and P amounts potentially stored in agricultural soils as crop residues, and nutrient loads from point sources generated in urban areas (Online Resource 2). The budget items per unit of area were calculated by dividing annual fluxes in each municipality by the corresponding UAA (kg N ha^{-1} year^{-1}, kg Si ha^{-1} year^{-1}, kg P ha^{-1} year^{-1}).

The uncertainty associated to the budget calculation was estimated by a Monte Carlo simulation. A normal probability distribution with a proper standard deviation was assumed for each coefficient used in the budgets to convert census data into nutrient amounts. Where a standard deviation was not available a uniform distribution was used to simulate coefficient between the minimum and maximum value of the target coefficient. A total of 1000 simulations were performed and for each simulation, a set of parameters was randomly generated from probability distribution functions. The budget calculation procedure was built in Excel, and R software (R Core Team 2017) was used to run the simulations. Uncertainties of budget terms are presented as means and upper (97.5 percentile) and lower (2.5 percentile) ranges of a 95% confidence interval. Uncertainties of model parameters were reported (in term of CV or ranges of values) in Online Resource 3 together with the description of the calculation procedure of each budget term. CVs of model coefficients were based on all the best available information for the investigated area. Otherwise, values commonly used in watershed nutrient budgeting studies were assumed.

Export of N, Si and P and internal processes in the Mincio River basin

The annual total nitrogen (TN), phosphorus (TP) and silica (TSi) loads were estimated from discharge and water chemistry data at Peschiera del Garda and Governolo, the outflowing section from the Lake Garda and the watershed outlet, respectively (Fig. 1). Flow data, dissolved (nitrate—NO_3-N, ammonium nitrogen—NH_4-N, dissolved organic nitrogen—DON, orthophosphate—PO_4-P, dissolved organic phosphorus—DOP) and particulate (particulate nitrogen—PN, particulate phosphorus—PP) concentrations of N and P were collected by the Regional Agency for the Environmental Protection (ARPA) (monthly data, from 1990 to 2010), while we measured seasonally dissolved silica (DSi) concentrations and flows from 2008 to 2010 (n = 16) in the research project "Definition of the minimal vital flow of the Mincio River". Amorphous silica (ASi) was estimated from total suspended solid (TSS) load (concentration × flow; data collected seasonally from 2008 to 2010, see above) multiplied by a conversion factor reported by Sferratore et al. (2006): ASi in TSS is 18.4 and 5.7 mg Si g^{-1} in summer and winter, respectively, to obtain the total annual ASi. The biogenic silica (BSi) fraction was calculated by converting the chlorophyll-*a* (Chl-a) concentration (data collected seasonally from 2008 to 2010; see above) into carbon by the C:Chl-a ratio (μg Chl-a L^{-1} × 40 = μg C L^{-1}; Cloern et al. 1995) and then by dividing for the C:Si theoretical Redfield ratio (106:15). BSi concentration was multiplied for water discharge to obtain daily load.

The mean annual TN and TP loads were calculated by multiplying monthly TN and TP concentrations by mean monthly water flow at Mincio River upstream and downstream extremes and then integrating the values to 1 year. Instead, to obtain TSi (= DSi + ASi + BSi) mean annual load, the same calculation was performed by using seasonal data which were integrated to 1 year.

The difference between the mean annual TN, TP and TSi loads at the watershed outlet (Governolo) and that measured at the outflowing section from the Lake Garda (Peschiera del Garda) can be defined as the net N, P and Si export from the Mincio River basin. We calculated the net mean annual river export for the decade 1990–2000 and 2001–2010. We applied the propagation of errors in the measured discharge and TN, TP and TSi concentration values to estimate the uncertainty in the net annual import and export of these nutrients to and from the Mincio watershed.

We also estimated the N amount permanently removed by denitrification in the aquatic ecosystems of the Mincio River basin, including the wetland areas, the riparian buffer zones, the drainage network, and the river itself. For wetland area we also calculated the contribution of N uptake by different primary producers in retaining N temporarily. Such estimates were based on the combination of experimental measurements previously performed in the studied area (Pinardi et al. 2009, 2011) and literature rates that were up-scaled to the whole watershed. Calculations are described in detail in Online Resource 4.

Results

N, Si and P concentrations in the Mincio River

Nitrate represented on average 95% of the dissolved nitrogen forms and 75% of TN in the Mincio River. The catchment was characterized by a widespread N-pollution, as demonstrated by the high NO_3-N concentrations measured in surface and groundwater (Fig. 3a). High levels of NO_3-N were measured in most of the Mincio River tributaries and in the high plain groundwater (Fig. 3a). The ARPA dataset showed for both investigated periods that NO_3-N concentrations increased from Peschiera del Garda

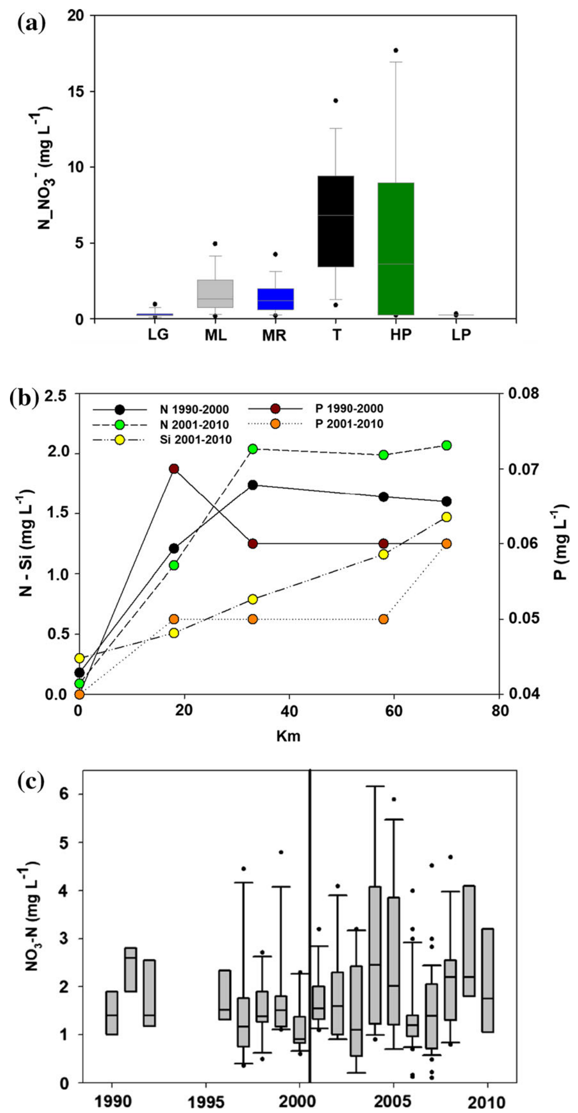

Fig. 3 Nutrient concentrations in the Mincio River basin. Panel **a** reports the boxplot of NO_3-N concentrations measured in different aquatic environments (LG = Lake Garda, n = 195; ML = Mantua Lakes, n = 467; MR = Mincio River, n = 1011; T = tributaries, n = 281; HP = high plain groundwater, n = 172; LP = low plain groundwater, n = 33) of the Mincio River watershed from 1990 to 2010. Panel **b** shows nutrient concentrations (median values of NO_3-N, PO_4-P, DSi) in the two macro-period analyzed along the Mincio River: Peschiera del Garda (km = 0), Pozzolo (km = 18), Goito (km = 33), Formigosa (km = 58) and Governolo (km = 70). Panel **c** reports boxplot of NO_3-N concentrations at Governolo site in the two macro-period considered (1990–2000, n = 64, left portion of the graph; 2001–2010, n = 142, right portion of the graph). (Color figure online)

(median 0.16 and 0.07 mg L^{-1} in 1990–2000 and 2001–2010, respectively) to Goito (median 1.36 and 1.80 mg L^{-1}, respectively), whereas they tended to decrease downstream the Mantua Lakes (Fig. 3b). Nitrate concentrations at the Mincio watershed outlet (Governolo) showed high variability during the year and no significant trend was found along the available historical data set (Fig. 3c).

Dissolved silica concentrations were available only for the period 2001–2010, and increased from upstream (median 0.28 mg L^{-1}) to downstream (median 0.89 mg L^{-1}) (Fig. 3b). The PO_4-P concentrations from the ARPA dataset nearly doubled from Peschiera del Garda (median 0.025 mg L^{-1} in both periods) to Governolo (median 0.060 and 0.050 mg L^{-1} in 1990–2000 and 2001–2010, respectively) (Fig. 3b). Nutrient stoichiometry at the watershed outlet suggested a generalized N excess and P limitation (N:P = 250; N:Si = 3.5; Si:P = 70).

N, Si and P soil budgets

In the Mincio River basin N, Si and P input terms exceeded outputs, with element-specific differences among sources and periods (Table 2; Fig. 4; Fig. 3 in Online Resource 1). Confidence intervals (95%) of each budget term are reported in Online Resource 3. Total N inputs to agro-ecosystems were estimated in over 26,000 t N in 2000, mostly sustained by manure spreading (42%, Table 2). In 2010 this percentage increased to 56%, due to a significant reduction of other inputs, in particular synthetic fertilizer distribution (− 54%) and biological fixation (− 21%). Inputs from synthetic fertilizers were the second main N source in 2000 (32% of the total), while in 2010 their contribution decreased to 18% and was lower than biological fixation (Table 2). Atmospheric N depositions were similar in both periods, contributing to < 3% of total N input (Table 2). Crop harvest represented the main process removing N from agricultural soils (∼ 70% of total input for both periods; Table 2). Total N inputs exceeded TN outputs by over ∼ 11,400 t N (on average 196 kg N ha^{-1} $year^{-1}$) and ∼ 7600 t N (on average 132 kg N ha^{-1} $year^{-1}$) in 2000 and 2010, respectively. Nitrogen excess decreased by 33% in a decade (Table 2).

Silica and P budgets were similar in the 10-year period (Table 2). Total Si and P inputs to agro-ecosystems were mainly sustained by livestock

Table 2 Nitrogen, silica and phosphorus budgets in the Mincio River basin for the years 2000 and 2010

	N budget				Si budget				P budget			
	2000		2010		2000		2010		2000		2010	
	t N $year^{-1}$	kg N ha^{-1} $year^{-1}$	t N $year^{-1}$	kg N ha^{-1} $year^{-1}$	t Si $year^{-1}$	kg Si ha^{-1} $year^{-1}$	t Si $year^{-1}$	kg Si ha^{-1} $year^{-1}$	t P $year^{-1}$	kg P ha^{-1} $year^{-1}$	t P $year^{-1}$	kg P ha^{-1} $year^{-1}$
Input												
Livestock manure	11,343	193.9	12,165	210.4	2101	35.9	2160	37.4	3183	54.4	3601	61.9
Synthetic fertilizers	8539	146.0	3886	67.2	0	0.0	0	0.0	989	16.9	510	8.8
Biological fixation	6507	111.2	5110	88.4	–	–	–	–	–	–	–	–
Atmospheric deposition	409	7.0	491	8.5	53	0.9	50	0.9	12	0.2	12	0.2
Σ input*	**26,798**	**458.1**	**21,652**	**374.5**	**2154**	**36.8**	**2210**	**38.2**	**4184**	**71.5**	**4122**	**70.8**
Output												
Crop harvest*	10,753	183.8	9960	172.3	**2147**	**36.7**	**2040**	**35.3**	**1693**	**28.9**	**1623**	**27.9**
NH_3 volatilization	2634	45.0	2465	42.6	–	–	–	–	–	–	–	–
Denitrification in soils	1964	33.6	1605	27.8	–	–	–	–	–	–	–	–
Σ output*	**15,351**	**262.4**	**14,031**	**242.7**								
Σinput − Σoutput*	**11,447**	**195.7**	**7621**	**131.8**	**8**	**0.1**	**170**	**2.9**	**2491**	**42.6**	**2499**	**42.9**
2.5%**	*7127*	*121.8*	*3597*	*62.2*	*− 877*	*− 15.0*	*− 606*	*− 10.5*	*1856*	*31.7*	*1827*	*31.6*
97.5%**	*16,058*	*274.5*	*11,734*	*202.9*	*796*	*13.6*	*776*	*13.4*	*3186*	*54.5*	*3207*	*55.5*

Data are expressed as tons of N, Si and P produced or consumed per year in the whole basin and normalized for the agricultural surfaces

*The summation values of input, output, and the difference beetwen them are reported in bold

**The confidence interval (2.5–97.5%) of the Soil System Budget is also reported in italic

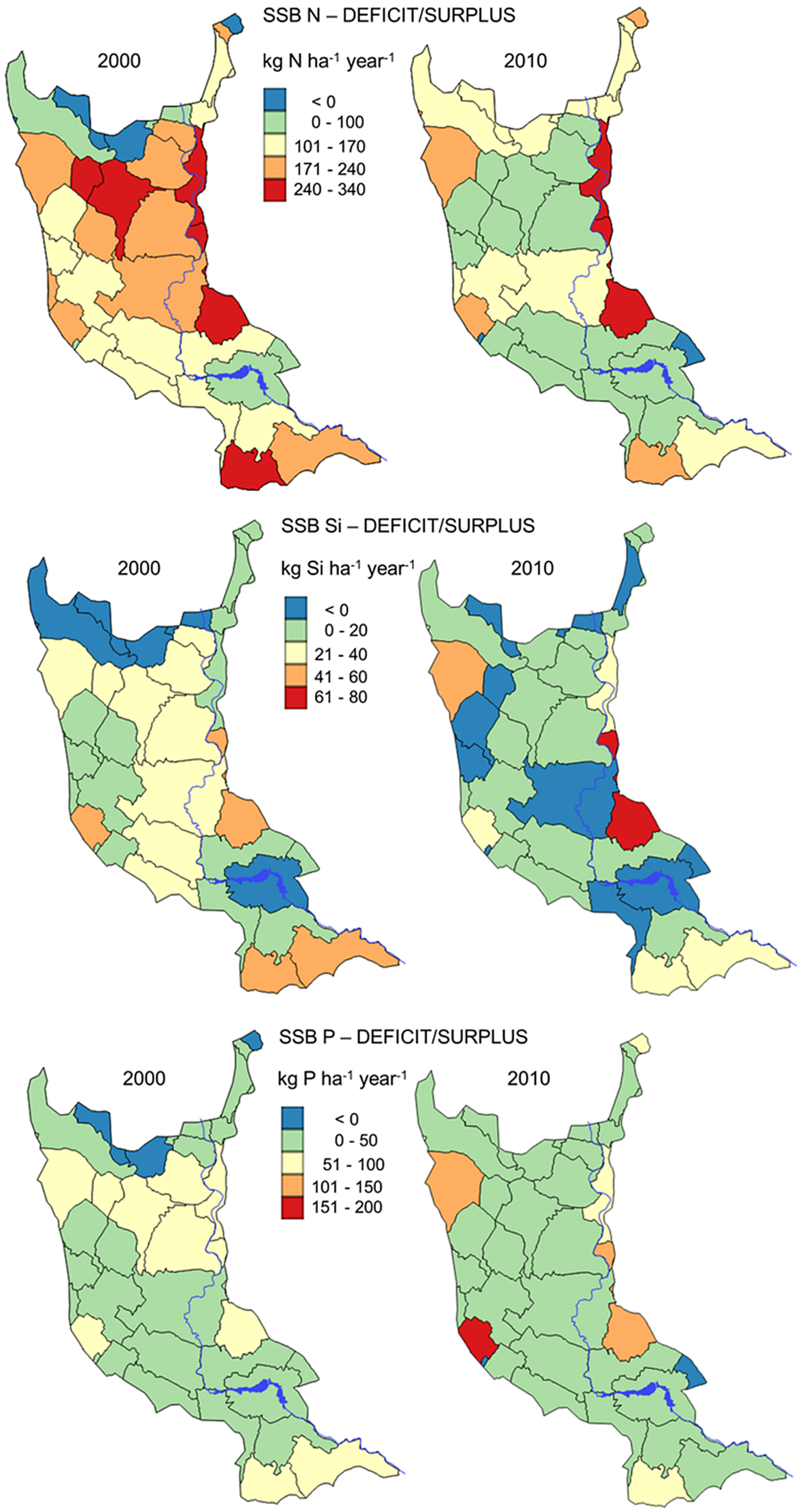

Fig. 4 Spatial distribution of N, Si, and P surplus/deficit obtained with the soil system budget (SSB) methodology. Values are expressed as kg ha^{-1} year^{-1}. (Color figure online)

manure (Si: ~ 98% for both years; P: 76% and 87% for 2000 and 2010, respectively; Table 2). As for N, the contribution of synthetic fertilizers to total P inputs decreased from 24 to 12%. Silica crop harvest was coupled with Si input from manure (95–100% in both years), while P crop harvest from agricultural soils was much lower (~ 40%) of TP inputs. Total P input from synthetic fertilizers decreased by 48% from 2000 to 2010.

Areal N, Si and P budgets in the different municipalities included both positive (surplus) and negative (deficit) values (N: from − 33 to 354 kg ha^{-1} $year^{-1}$; Si: from − 79 to 45 kg ha^{-1} $year^{-1}$; P: from − 10 to 148 kg ha^{-1} $year^{-1}$; dataset: 2000 and 2010) (Fig. 4). Maps show a generalized decrease of N inputs and surplus in the basin from 2000 to 2010 (Figs. 4 and 3 in Online Resource 1). Silica inputs and outputs increased from 2000 to 2010, and rates were elevated in the municipalities where livestock population was greater (Fig. 3 in Online resource 1). The Si budget resulted in a general reduction of the surplus up to a deficit in the majority of municipalities from 2000 to 2010 (Fig. 4). In 3 out of 38 municipalities, Si surplus increased due to the increase in number of swine and therefore in Si inputs by manure (Fig. 4). From 2000 to 2010, P inputs decreased in the high plain municipalities and remained constant in the rest of the basin, with the exception of 6 municipalities where P inputs increased (Fig. 3 in Online resource 1). This was coupled to a general increase in P outputs in the westernmost municipalities of the Mincio basin. P budgets at the basin level were similar between the two decades; only in 4 municipalities an increase of P surplus was detected (Fig. 4).

In all nutrient budgets, the dominant output term was uptake by cultivated crops, that upon harvesting results in the net removal of organic N, Si and P stored in the aboveground crop biomass. Our uptake term does not include the belowground nutrients that remain in the soils and are recycled. N and P availability in agricultural soils in the form of crop residues were estimated in 3300–3600 t N $year^{-1}$ (50% as cereal straw) and ~ 560 t P $year^{-1}$ (70% as cereal straw). Silica was also stored into cereal straw (~ 2700 and ~ 3150 t Si in 2000 and 2010, respectively), and generally harvested and used as litter for cattle.

In the 10-year period, the human population in the Mincio River basin increased by 13%, from ~ 184,000 to ~ 207,000 units. N loads from urban area were estimated in 840 t N $year^{-1}$ in 2000 and 946 t N $year^{-1}$ in 2010. P loads were 121 and 136 t P $year^{-1}$ in the first and in the second decade, respectively. Moreover, the Mincio River basin hosted ~ 130,000 equivalent population for industrial activities and the N and P loads potentially generated were ~ 630 t N $year^{-1}$ and ~ 83 t P $year^{-1}$, respectively. Instead, Si loads from urban sources were low and estimated in < 1 t Si $year^{-1}$ in both decades.

The stoichiometry of N, Si and P surplus in agricultural soils suggests a strong potential limitation of Si but also a potential N limitation in aquatic ecosystems where these nutrient excess might be delivered, with N:Si molar ratios always ≫ 50 and N:P molar ratios of 10 and 7 in 2000 and 2010, respectively.

N, Si and P export from the Mincio basin

The net TN export (= downstream (Governolo)-upstream (Peschiera del Garda) loads) from the Mincio basin was 380 ± 601 (6 ± 10 kg N ha^{-1} $year^{-1}$) and 2071 ± 653 t $year^{-1}$ (36 ± 11 kg N ha^{-1} $year^{-1}$), representing 3% and 27% of the N surplus calculated for the decades 1991–2000 and 2001–2010, respectively (Table 3). Dissolved N was the main form of exported TN, with NO_3-N as the dominant ion, increasing its concentrations along the river course and resulting in net accumulation and export at the Mincio watershed outlet (Table 3). In contrast, NH_4-N was assimilated or transformed along the river course, and its aquatic budget was negative in both the considered periods (Table 3). From the first to the second analyzed decade, the net export of NO_3-N and PN increased by 115% and 65%, respectively. This was coupled to a lower NH_4-N retention along the river (− 68%). This data can be explained considering that at Peschiera del Garda TN loads decreased by 35% from the first to the second period analyzed (NO_3-N and NH_4-N decreased by 66 and 53%, while PN increased by 65%), while at Governolo TN loads increased by 68% (all forms of N increased: NO_3-N by 71%, NH_4-N by 45% and PN by 65%). The difference between N surplus and export was ~ 11,070 t $year^{-1}$ in 2000 and ~ 5550 t $year^{-1}$ in 2010.

The load of TSi at Peschiera del Garda and Governolo were 324 ± 117 and 1798 ± 479 t $year^{-1}$ for the period 2001–2010, respectively (no data

Table 3 Net nutrient export (= downstream-upstream loads) from the Mincio River basin to the Po River

	Net export: 1990–2000				Net export: 2001–2010			
	Mean* t $year^{-1}$	SD**	Mean kg ha^{-1} $year^{-1}$	SD	Mean t $year^{-1}$	SD	Mean kg ha^{-1} $year^{-1}$	SD
TN	**380**	*601*	**6**	*10*	**2071**	*653*	**36**	*11*
NO_3-N	**944**	*471*	**16**	*8*	**2037**	*576*	**35**	*10*
NH_4-N	**− 725**	*340*	**− 12**	*6*	**− 232**	*111*	**− 4**	*2*
PN	**161**	*155*	**3**	*3*	**266**	*286*	**5**	*5*
TSi	–	–	–	–	**1474**	*493*	**25**	*8*
DSi	–	–	–	–	**1018**	*450*	**17**	*8*
BSi	–	–	–	–	**314**	*187*	**5**	*3*
ASi	–	–	–	–	**142**	*74*	**2**	*1*
TP	**20**	*17*	**0.35**	*0.30*	**45**	*32*	**0.77**	*0.55*
PO_4-P	**6**	*16*	**0.10**	*0.27*	**16**	*25*	**0.3**	*0.4*
PP	**14**	*7*	**0.25**	*0.12*	**29**	*21*	**0.5**	*0.4*

The export was calculated for two macro-periods (1991–2000 and 2001–2010). Data are expressed as tons of N, Si and P per year and normalized per area of agricultural land (*TN* total nitrogen, *NO_3-N* nitric nitrogen; *NH_4-N* ammonium nitrogen; *PN* particulate nitrogen; *TSi* total silica; *DSi* dissolved silica; *BSi* biogenic silica; *ASi* amorphous silica; *TP* total phosphorus; *PO_4-P* orthophosphate; *PP* particulate phosphorus)

*Mean values are reporter in bold

**Standard deviation (SD) values are reported in italic

available for the decade 1991–2000), resulting in a net export of Si from the catchment of 1474 ± 117 t $year^{-1}$ (25 ± 8 kg Si ha^{-1} $year^{-1}$) (Table 3), nearly one order of magnitude higher compared to Si surplus. This export consisted mainly of dissolved silica (69% of TSi), followed by BSi and ASi (21% and 14% of TSi, respectively). Exported DSi and Bsi had an opposite seasonal pattern, with a DSi minimum (6 ± 32 kg day^{-1}) and a BSi maximum (105 ± 118 kg day^{-1}) in spring and a DSi maximum (473 ± 14 kg day^{-1}) and BSi minimum (31 ± 37 kg day^{-1}) in autumn.

At Governolo the net export of TP was 20 ± 17 t $year^{-1}$ (0.35 ± 0.30 kg P ha^{-1} $year^{-1}$) and 45 ± 32 t $year^{-1}$ (0.77 ± 0.55 kg P ha^{-1} $year^{-1}$) in the first and second period considered, respectively (Table 3). Such net export represented a minor fraction (nearly 2%) of the annual P surplus in the agricultural soils, suggesting large retention within the basin. The main form of exported TP was the particulate one, contrary to N and Si. All the P forms doubled or more than doubled from the first to the second decade analyzed (Table 3).

Discussion

N, Si and P soil budgets

The exceedance of total inputs of N and P above crop requirements to the agro-ecosystems of the Mincio watershed highlights N and P pollution risk for aquatic ecosystems in this area, which is supported by high NO_3-N (but not PO_4-P) concentrations in the river, in Mantua Lakes and in their tributaries. Silica budgets revealed instead a general equilibrium between input and output terms in both periods. Areal N inputs and surplus obtained in the Mincio basin municipalities are among the highest reported for other agricultural areas in Europe and North America and calculated at different spatial scales with comparable methods (Vagstad et al. 2004; Sobota et al. 2009; de Vries et al. 2011; Lassaletta et al. 2012; Hou et al. 2015; Özbek and Leip 2015). With respect to the Italian context, the average areal N surplus of the Mincio River basin (196 and 132 kg N ha^{-1} $year^{-1}$, for 2000 and 2010, respectively) was higher than that reported for a deltaic watershed (Po di Volano, ~ 60 kg N ha^{-1} $year^{-1}$), where synthetic fertilizers dominated the N inputs to agricultural soils (Castaldelli et al.

2013). Nitrogen surplus in the Mincio was similar to that calculated for the neighboring Oglio River basin (125 and 180 kg N ha^{-1} year^{-1}, for 2000 and 2008, respectively; Bartoli et al. 2012), and in the range reported for Western Po plain (Piedmont, Italy; 128–335 kg N ha^{-1} year^{-1} in Grignani and Zavattaro 2000; pp. 40–320 kg N ha^{-1} year^{-1} in Sacco et al. 2003). Elevated N surplus in the Po River basin is generally associated to high livestock densities and high availability of manure to be spread (e.g. Vagstad et al. 2004). Despite a decrease from 2000 to 2010, in most municipalities N inputs exceeded the limit set by the Nitrates Directive in vulnerable (170 kg N ha^{-1}) and non-vulnerable soils (340 kg N ha^{-1}).

Silica input to agro-ecosystems increased by 3% from 2000 to 2010 due to an increase in livestock manure availability (the number of swine increased by 20%), and to a reduction in Si crop harvest (− 5%), due to lower surfaces cultivated with high demanding Si crops. Average watershed P surplus ($\sim$ 43 kg P ha^{-1} year^{-1}, for both periods) was in the range reported for other agricultural areas in Northern Italy (Sacco et al. 2003; Bassanino et al. 2011), even if some municipalities exceeded the previously published values, and was higher than P surplus reported for watersheds in the Baltic area (up to 13 kg P ha^{-1} year^{-1}, Vagstad et al. 2004).

Looking at crop types, from 2000 to 2010, surface areas planted in cereal grains increased by 9%, while industrial crops and horticulture and woody crops decreased by 5 and 3%, respectively. Moreover, surface area cultivated by N-fixing crops declined by 30% in the second decade, substituted by N demanding crops (i.e. cereals). However, N surplus decreased from 2000 to 2010 due to a significant reduction of synthetic fertilizer application (− 54%). Such reduction is likely due to increasing costs and to the restrictions imposed by EU Nitrates and Water Framework Directives (Sileika et al. 2006).

The municipalities with the highest nutrient surplus are characterized by large livestock populations, and are located in three different portions of the watershed: (i) Lonato, Castiglione delle Stiviere, and Valeggio sul Mincio in the high plain, (ii) Goito, Marmirolo, and Piubega in the medium plain, and (iii) Borgoforte and Bagnolo S. Vito in the low plain (see Fig. 1 for municipality location). In the high plain, due to gravel soils, a high water quantity (up to 4500 m^3 ha^{-1} year^{-1} by flooding and up to 3200 m^3 ha^{-1} year^{-1} by sprinkler) is used to irrigate cereals, in particular maize, and fruit trees, the main crops in this portion of the basin. In the medium plain, in particular in Goito and Marmirolo, permanent meadow and cereals, the main crops, are irrigated by flooding due to large water availability and permeable soils by using on average 3500–5500 m^3 ha^{-1} year^{-1} of water. In the high and medium plain N surplus, irrigation practices and soil permeability result in high risk of NO_3-N pollution in aquatic environments (Laini et al. 2011). Large water infiltration during the irrigation period (April–September) causes a significant rise of the shallow aquifer water table and fastens the mobilization of nutrient excess to surface and groundwater (Bartoli et al. 2012). In areas with similar hydrological alterations, Balderacchi et al. (2016) have demonstrated how fast pollutants reach surface aquatic bodies through rapid groundwater flushing. This is a peculiarity of a large portion of the Po River basin, due to a combination of large water availability and highly permeable soils. In the low plain, cereals and alfalfa are the main crops irrigated by sprinkler technique (up to 3900 m^3 ha^{-1} year^{-1} of water) and are associated to high livestock density. Despite this potential nutrient pollution from agricultural lands, the vulnerability of this portion of the basin is low due to the clays and silts composition of soils.

Export of N, Si and P and internal processes in the Mincio River basin

In-stream N, Si and P loads measured in the Mincio River appeared to be mostly generated by agricultural and farming activities, as suggested by the comparison with potential sources from urban and industrial areas. N, Si and P loads generated by the human population represented as a whole $\sim$ 4%, $\sim$ 0.1% and $\sim$ 3% of the total N, Si and P input to agricultural lands, respectively. Moreover, such percentages are probably overestimated, as $\sim$ 100% of the municipality sewage systems are connected to wastewater treatment plants with tertiary treatments that remove up to 70–80% of the incoming N and P loads via denitrification and chemical dephosphatation, respectively (Report on Environmental Status published in 2006 by ARPA Lombardy). Therefore, nutrient loads from urban areas entering directly into the drainage network of the Mincio watershed were negligible in comparison to diffuse loads.

At the basin scale, 3 and 27% of the N surplus was exported to the Po River in 2000 and 2010, respectively, and the fate of about 11070 and 5550 t N year^{-1} remained therefore unaccounted. Nitrogen can be stored in agricultural soils, due to a mismatch between crop fertilization and crop harvest or as crop residues (Grimvall et al. 2000; Kroeze et al. 2003). In the Mincio watershed, the N amount stored in crop residues was estimated in 29–47% of the N surplus, but about 50% of residues is cereal straw, which is usually removed from the fields and used as bovine litter, and then recycled to the agricultural soils through the final disposal of livestock manure. Missing N can be explained by other pathways or internal processes such as N accumulation and denitrification in groundwater (Delconte et al. 2014; Martinelli et al. 2018) and N removal in drainage and irrigation canals (Castaldelli et al. 2015; Soana et al. 2017), riparian buffer strips (Dalgaard et al. 2014), and wetlands (Passy et al. 2012; Hansen et al. 2018). We estimated the amount of N retained or permanently removed in the aquatic ecosystems of the Mincio river basin, including the wetland areas, the drainage network and the associated riparian buffer zones, and the river itself. Temporary (assimilation) and permanent (denitrification) N removal in the Mincio wetland area was estimated in up to 2600 t N year^{-1}, with the contribution of uptake varying between 736 and 1703 t N year^{-1}, and that of denitrification varying between 367 and 906 t N year^{-1}. Denitrification in the drainage network and the associated riparian buffer zones was estimated in up to 2790 and 564 t N year^{-1}, respectively, while denitrification in the Mincio River course represented a minor N loss term (up to $\sim$ 182 t N year^{-1}). Such preliminary estimates suggest that the drainage network and the wetland may significantly mitigate the N surplus generated in the watershed. The wetland area in the Mincio basin ($\sim$ 2200 ha including the fluvial lake system of Mantua, $\sim$ 3% of watershed area), even if low in absolute terms, is one order of magnitude higher compared to wetland areas within other agricultural basins of the Po Plain context (Bartoli et al. 2012).

Nitrogen input to soils, and therefore N surplus, decreased from 2000 to 2010, but nitrate concentrations at the Mincio watershed outlet did not follow the same pattern. Elsewhere similar results were found, with large lags between reduction in N inputs and reduction of N export, due to slow mineralization and release of organic N stored in soils (Bouraoui and Grizzetti 2011; Chen et al. 2014b; Van Meter and Basu 2015). Large N export despite significant decrease of synthetic fertilizers inputs is a surprising result for the considered basin that was expected to react promptly to reduction in N inputs. In the high and medium plain of the Mincio watershed in fact, flood-based irrigation practices and gravel soils were supposed to favor fast mobilization of the more soluble N forms from terrestrial to aquatic environments both by percolation and by surficial runoff. During summer the steep increase of NO_3-N concentrations in upstream reaches without point sources (i.e. from km 18 to km 33; Fig. 3b), supports fast NO_3-N mobility from groundwater to river. The underlying mechanisms seems driven by the irrigation loop: flooding permeable soils causes percolation of nitrate-rich waters, which feed shallow aquifers; in turn, they migrate vertically and supply the riverbed with nitrate-rich waters. The irrigation loop is supported by findings of Perego et al. (2012) and Balderacchi et al. (2016) that report for several sites within the Po plain, including the Mincio basin, that N losses change seasonally depending on N inputs to farmland and irrigation practices. High N export despite N inputs reduction suggest that other mechanisms besides irrigation regulate the transfer of N from terrestrial to aquatic compartments, among which the interannual climatic anomalies. Precipitation patterns and intensity for example may affect soil water saturation and rates of soil denitrification, with large differences in dry or wet winters (Ramoska et al. 2011).

Total Si discharged by the Mincio River into the Po River was large (1724 $\pm$ 576 kg Si km^{-2} year^{-1}) and more than doubled the values reported by Amann et al. (2014) for the Elbe Estuary ($\sim$ 700 kg Si km^{-2} year^{-1}; 148,268 km^2; Germany) and by Carbonnel et al. (2009, 2013) for the tributaries of the Scheldt tidal River ($\sim$ 940 kg Si km^{-2} year^{-1}; 21,860 km^2; Belgium/The Netherlands). In the period 2001–2010, TSi export outside the Mincio watershed was higher than the Si surplus, suggesting unaccounted for input terms from agriculture or large erosion and losses of mineral silica from soils. The coupled terrestrial-aquatic Si cycle is understudied as compared to N and P and input–output terms are affected by a large degree of uncertainty. A large Si amount for example is stored in crop residues, but the fraction in cereal straw should return to agricultural land via livestock manure spreading. Dissolved Si concentrations increased from upstream to downstream, suggesting diffuse input of this element from the watershed, but more data are necessary (i.e. silica loads during flood events or during the irrigation period in areas were flooding practices are prevailing, when the particulate fraction may become significant). As an example, Smis et al. (2011) reported that on an annual basis ASi transport was up to 40% of total Si load. Future studies should target at measuring the ASi fraction for all compartments, TSi contribution of point sources (i.e. tributaries), and estimating diffuse nutrient loss (erosion, runoff, leaching) from agricultural soils to the river. A portion of the unaccounted TSi can be also explained by river-groundwater interaction, as reported by Clymans et al. (2013) for a small forested Belgian catchment.

With respect to P, only 1–2% of agricultural excess was exported from the watershed by river discharge, mainly in the particulate form, suggesting significant retention of P in the Mincio basin. Internal P sinks include crop residues, that contain an organic P pool estimated in $\sim$ 22% of P surplus (Chen et al. 2015). However, the annual TP load calculated from the available hydrochemical datasets includes only baseflow conditions and probably underestimates the real P export. Indeed, flood events usually mobilize a large fraction of particulate P (Bowes and House 2001; Carpenter et al. 2015). It is also true that the Mincio River is regulated and high discharge periods are infrequent due to the buffer action of the Lake Garda (see www.laghi.net for historical discharge data). The retained P can be potentially transported and stored in groundwater, a pathway which is actually understudied (Holman et al. 2008; Rasiah et al. 2011; Elliott and Jaiswal 2012). The Mantua Lakes and the surrounding wetland areas can explain part of the P retention in the Mincio basin. In fact, P removal and both short-term uptake and long-term permanent storage by wetlands are determined by several mechanisms such as physical input rates and retention times, chemical reactions, as well as biological uptake (Bennett et al. 2001; Johannesson et al. 2011). Such mechanisms in the Mincio seems favoured by the steep reduction of water velocity in the proximity of Mantua lakes, promoting suspended solids sedimentation. Further investigation on sediment accumulation can improve the understanding of mechanisms underlying P retention.

Nutrient stoichiometry

Results from this study, despite uncertainties associated to budget terms, suggest that the stoichiometry of nutrient excess in soils is not reflected by the stoichiometry of nutrients exported with discharge outside the basin. In other words, element-specific mechanisms affect differentially the delivery of nutrients from agricultural areas, and the transformations of nutrients within aquatic ecosystems. Within these element-specific mechanisms, we believe that the irrigation loop, in particular in the high and medium plain, plays a major role as driver of N and Si vertical and horizontal transfer and that the retention of P is favored by limited erosion in the mostly plain basin. Within the aquatic ecosystem, in particular coinciding with the steep reduction of water velocity in the Mantua Lakes, dissolved nutrients are converted into primary producers biomass and accumulated together with particulate inorganic forms in sediments (Laini et al. 2011; Balderacchi et al. 2016; Pinardi et al. 2011, 2014; Bertani et al. 2016).

Assuming nutrient excess in soils is a proxy of N, Si and P quantitative transfer to aquatic ecosystem, the stoichiometry of surplus indicated N and Si as potentially limiting algal growth. Such prediction was not validated as both nutrients were abundant in the Mincio waters and their loads increased along the river course. At the Mincio watershed outlet (Governolo) N:P molar ratio increased from the first to the second decade (from $\sim$ 80 to $\sim$ 250), rather suggesting P limitation. In the second decade, where Si data are available, Si:P ($\sim$ 70) and N:Si ($\sim$ 3.5) molar ratios confirm P limitation, and suggest a relatively balanced N:Si stoichiometry. Along the whole Mincio River course N:P ratio was close or lower than the Redfield ratio only in Peschiera del Garda (upstream site; N:P = 14 and 6 in 2000 and 2010, respectively) (Fig. 5a,b). Downstream, with some variability among the two macroperiods, a strong increase of N:P ratio was always recorded, up to 80 in Goito (km = 33) (Fig. 5a, b). Similar trend in nutrient ratios were recorded during irrigation and non-irrigation periods, suggesting that diffuse inputs to the river peaked in the high and medium plain (Fig. 5a, b). Also N:Si ratio was close to the theoretical value only upstream, while downstream the increase of NO_3-N was proportionally higher than that of Si, with a ratio increase up to 6 in Goito and then a

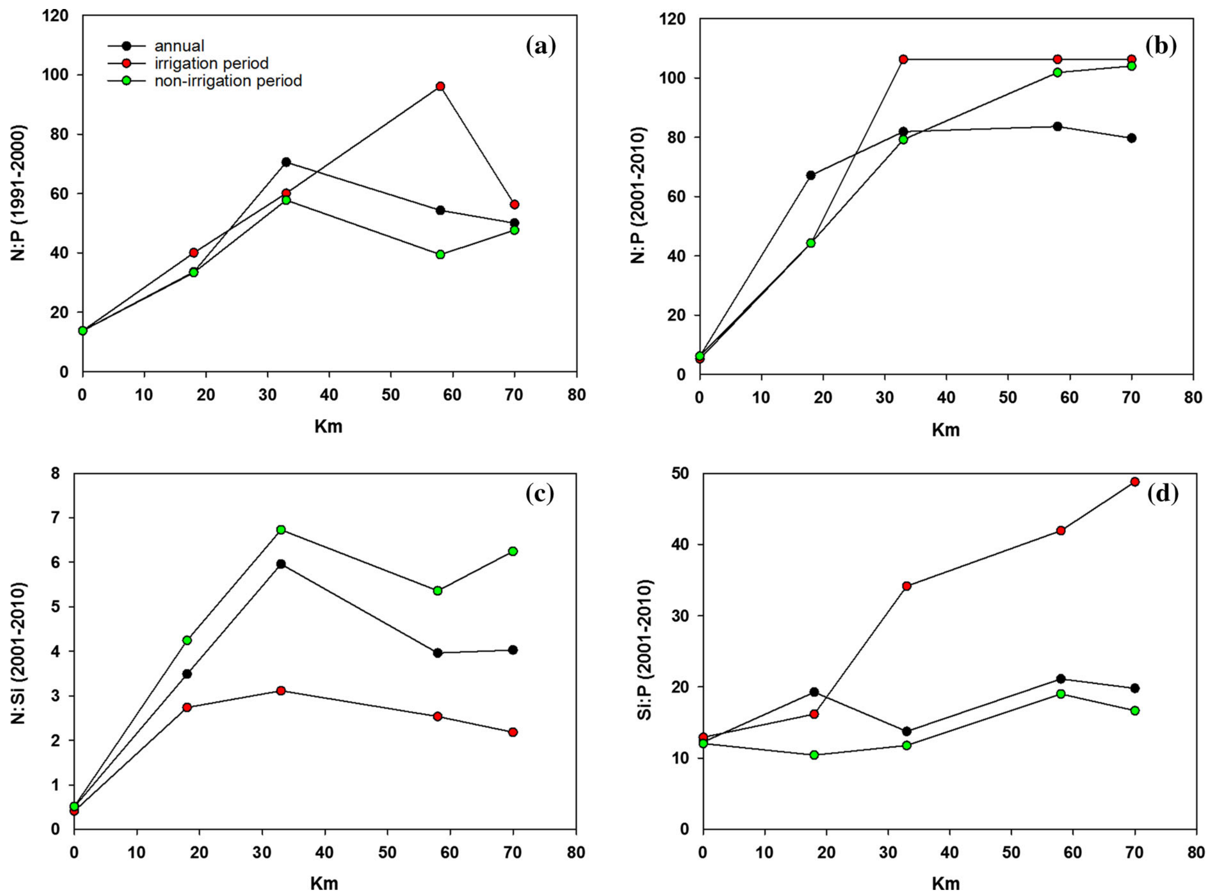

Fig. 5 Nutrient stoichiometry on annual basis and for the irrigation and non-irrigation periods along the Mincio River. N:P ratio was reported for the periods 1991–2000 (**a**) and 2001–2010 (**b**). N:Si (**c**) and Si:P (**d**) ratios were reported only for the second decade. Dashed lines represent the theoretical ratios. Peschiera del Garda (km = 0), Pozzolo (km = 18), Goito (km = 33), Formigosa (km = 58) and Governolo (km = 70). (Color figure online)

decrease to 4 downstream the Mantua lakes (Fig. 5c). The N:Si and Si:P ratios showed a strong seasonal difference, mainly due to higher Si and lower PO_4-P concentrations in the irrigation period, suggesting a clear P limitation, as also confirmed by the N:P ratio (Fig. 5c, d).

In the Mincio River a generalized N (and Si) excess over P suggest a little risk for non-siliceous algal blooms in the Mantua lakes, even if the occurrence of cyanobacteria during late summer is reported for recent years (Bresciani et al. 2013, 2017). In contrast, in the Nemunas watershed (Baltic area), where agriculture is not irrigated, the ecological stoichiometry of exported nutrients undergoes a clear seasonality, with pronounced N excess during winter and N and Si limitation during summer. Such seasonality likely drives the shift in the composition of algal assemblages, from diatoms in winter-spring to cyanobacteria in the summer (Vybernaite-Lubiene et al. 2017).

Conclusions

Our outcomes suggest that the simultaneous analysis of N, Si and P, rather than of single elements, allows better understanding the different paths, transformation and retention mechanisms at the whole watershed level. Nutrient stoichiometry in terrestrial areas, together with element-specific processes during the path from agricultural land to surface or groundwater, have important consequences on nutrient loads transported by the canal network and exported by rivers. In particular, the irrigation loop may play an important role in increasing N and Si transfer from terrestrial to aquatic habitats. Future ecological studies in this field should increase our knowledge on Si and in particular investigate additional sources of this element, and the transformation and transport pathways it undergoes both in agricultural lands and in inland waterbodies. Unbalanced N:Si:P ratios in inland waters have critical implications for algal communities composition both in freshwater and in coastal areas.

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