Recent evolution and expected changes of nutrient loads in a heavily exploited watershed: the Po River, Italy

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Abstract The Po River watershed accounts for about 25% of the total surface and about 40% of the gross domestic product of Italy. Agricultural, industrial and urban development, along with hydromorphological modification of rivers and canals, are responsible for water quality deterioration. Frequent and persistent summer droughts and extreme floods have occurred concurrently in the last two decades, likely as early signals of exacerbation of global change effects. In this contribution we review the evolution of hydrological regime and nutrient loadings in the last three decades, short-term studies (2003–2007) on the effects of persistent drought conditions on river discharge, nutrient loadings and stoichiometry, and salt wedge intrusion. To date, diffuse nitrate contamination has been one of the major threats. We identified and assessed possible nitrogen sources in the watersheds of four tributaries of the Po River (Parma, Mincio, Oglio and Po di Volano) with different livestock pressure, crop production and population densities.

Key words nutrients loadings; nutrient stoichiometry; river discharge; extreme hydrological events; agriculture; livestock

INTRODUCTION

Material fluxes from watersheds to the adjacent ocean reveal the growing pressure of anthropogenic activities on water quality and processes within aquatic ecosystems (Meybeck & Vörösmarty, 2005). The water quality and ecological status of the different water bodies may thus reflect the watershed–aquatic ecosystem interactions, particularly the impact of human activities at the river-basin scale, and interactions between biogeochemical cycles (Howarth *et al.*, 2011). Among others, one of the most important threats is nitrogen contamination (Grizzetti *et al.*, 2012).

In this contribution we review the evolution of water quality in the Po River basin, one of the most threatened watersheds in Europe. The evolution of nutrient loadings and their stoichiometry, especially nitrate contamination, are discussed in relation to hydrology, addressing the effects of extreme hydrological events. Relationships between land uses and nitrate contamination are also analysed in the watersheds of four tributaries of the Po River (Parma, Mincio, Oglio and Po di Volano) with different livestock pressure, crop production and population densities in order to identify the main pollution sources.

THE PO RIVER BASIN: FEATURES AND PROBLEM STATEMENT

The Po River, one of the major rivers in the Mediterranean region, is 652 km long with a 74 000 km^2 watershed, of which 71 057 km^2 is in Italy (Fig. 1). The average discharge is 1470 $m^3 s^{-1}$ (Zanchettin *et al.*, 2008). The hydrographic network comprises of 141 tributaries and approximately 50 000 km of artificial canals. Along the southern river bank, streams with an extremely variable flow regime drain from Apennine and Western Alp ridges. Along the northern river bank, four large and deep subalpine lakes (Maggiore, Como, Iseo and Garda), fed by Alpine glaciers, account for a water volume of approx. 17 km^3, nearly 70% of the total surface freshwater in Italy. These deep lakes feed the four main tributaries of the Po River (Ticino, Adda, Oglio and Mincio rivers, respectively) which make up about 50% of its total water discharge.

The human population remained nearly constant (~17 million) over the last three decades, with densities up to 1478 inhabitants km^{-2} in the Milan district and 25 inhabitants km^{-2} in the upper Alpine and Apennine valleys. Since 1960, the lowland urban areas have been growing exponentially at rates up to 20 ha d^{-1}, with peaks up to 200% in the most densely urbanized areas (Dall'Olio & Cavallo, 2009).

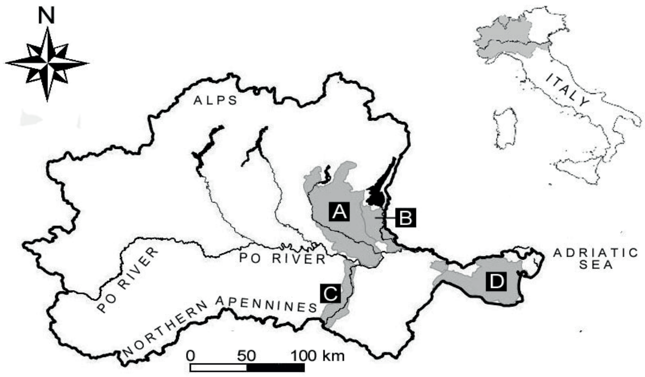

Fig. 1 Map of the Po River basin with indicated the sub-basins of Oglio (A), Mincio (B), Parma (C) and Po di Volano (D) rivers.

The Po River basin accounts for about 40% of the Italian GDP and 48% of the domestic energy demand. Its contribution to different sectors of GDP is 37% for industry, 35% for agriculture and 55% for livestock. The lowland is almost completely exploited for agriculture, urban areas and infrastructure. Rivers and streams are human-regulated for irrigation purposes and power generation. Agriculture is performed in ~43% of the total watershed surface, whilst the livestock is mainly concentrated in the central part of the watershed. Nearly 22 km^3 $year^{-1}$ of water are used for irrigation, which represents ~50% of the mean annual Po River discharge and roughly corresponds to the summer water flux in wet years.

Water pollution is a growing concern, which is estimated to be generated by 114 million inhabitant equivalents: 15% from urban sources, 52% from industrial activities and 33% from agriculture and livestock. Pesticides, solvents, DDT, PCB, PAH and metals were found in sediment and biota, along with drugs and pharmaceuticals, especially downstream of the main urban centres and in the lowland sectors of the river (Camusso *et al*., 1999; Calamari *et al*., 2003; Vignati *et al*., 2003). Phosphorus inputs were a major threat for inland and coastal waters from the 1960s to the 1980s (Vollenweider, 1992). Since the early 1990s, nitrogen pollution, especially nitrate, became the main concern for surface waters, groundwater (Cinnirella *et al*., 2005) and transitional waters (Viaroli *et al*., 2010).

The Po River bed has naturally undergone wide variations, but since the Second World War it has been greatly altered by damming, levee building, sand and gravel quarrying, and water withdrawal (Rinaldi *et al*., 2010). The main consequences are downstream erosion and riverbed deepening, on average 4–5 m with peaks of 10 m, causing changes from braided to single river-beds, narrower channels, and decreased connectivity between the riverbed and floodplain (Lamberti, 1993). In the lowland sector of the watershed, the floodplains of the Po River and its tributaries were originally composed of a number of wetlands, oxbow lakes and marshes, which contributed a biogeochemical buffering capacity, e.g. coupled nitrification–denitrification processes (Racchetti *et al*., 2011), along with a rich floral and faunal biodiversity (Bolpagni *et al.*, 2012). Nowadays, only relict remains are preserved thanks to the enforcement of Natura 2000. However, the lack of connectivity with rivers is likely to be a potential threat for their persistence.

HYDROLOGICAL REGIME AND NUTRIENT LOADINGS

The hydrological regime was studied over a time scale of about two centuries by Zanchettin *et al.*, (2008), who found evidence of a great interannual variability due more to hydraulic regulation of the hydrographic network than to climatic factors. Since the beginning of the 20th century, hydrological extremes have progressively amplified and early signals of possible effects of climate changes have occurred in the last two decades, when huge floods (1994 and 2000) were followed by extreme drought conditions. Of the five low flow extremes observed in the last 100 years, three

Table 1 Annual mean water discharge (Q), and annual loadings of soluble reactive phosphorus (SRP), total phosphorus (TP), dissolved inorganic nitrogen (DIN), total nitrogen (TN), and molar TN:TP and DIN:SRP ratios.

Year	Q[#] (m^3 s^{-1})	SRP (t P $year^{-1}$)	TP (t P $year^{-1}$)	DIN (t N $year^{-1}$)	TN (t N $year^{-1}$)	TN:TP molar	DIN:SRP molar
1968-70[x]	1378	1825	ND	53 028	ND	ND	62
1982-87*	1394	5319	12221	106 562	ND	ND	44.4
1988-90*	1362	3978	7300	118 900	144 175	43.7	66.2
1991-93*	1495	3650	9855	117 165	163 885	36.8	71.1
1995-96*	1596	3310	5770	136 100	147 200	56.5	91.0
1999[+]	1433	3739	10238	96 398	112 682	24.4	57.1
2000[+]	1966	2708	17056	153 625	180 723	23.5	125.6
2001[+]	1737	2579	7708	112 095	131 816	37.9	96.2
2002[+]	1931	3388	8382	146 549	179 701	47.5	95.8
2003[+]	1024	1762	5426	86 244	101 607	41.5	108.4
2004[+]	1436	2512	9334	134 301	156 300	37.1	118.4
2005[+]	941	1674	7388	87 222	102 706	30.8	115.4
2006[+]	922	1723	6326	77 942	87 650	30.7	100.2
2007[+]	833	1542	5453	61 434	71 512	29.0	88.2

Data from (x) Marchetti *et al*. (1989), (*) Provini & Binelli (2006), (+)Naldi *et al.*(2010), and (#) Hydrological Annals of the Environmental Agency of the Emilia-Romagna Region (http://www.arpa.emr.it). ND: not determined.

occurred between 2003 and 2006. Even if it is not possible to identify any evolutionary trend based on short time series, discharge data for the period 1991–2007 indicate a recurrent variability of the hydrological regime (Table 1).

Data on loadings of total nitrogen (TN), total phosphorus (TP), dissolved inorganic nitrogen (DIN = NO_3-N +NO_2-N+NH_4-N) and soluble reactive phosphorus (SRP) are available since 1982 (Table 1). Standard analytical methods were used. Details are reported in the references quoted in the table. Data on DIN and SRP are also available for 1968–1970 (Marchetti *et al.*, 1989; Justic *et al.*, 1995). The total phosphorus load underwent a marked interannual variability, with a peak of 17 056 t $year^{-1}$ in 2000, mainly due to the huge and persistent autumn flood, and minimum values of ~5400 t $year^{-1}$ in the dry years of 2003 and 2007. TN followed a similar pattern, with peaks up to 180 700 t $year^{-1}$ in wet years and values about 50% lower in the driest years. Both SRP and DIN (81–95% nitrates) increased sharply from the 1960s to 1980s, then progressively decreased, especially in the dry period 2005–2007.

The molar TN:TP = 36.6 ± 9.7 was nearly constant, whilst the DIN:SRP ratio increased from less than ~60 before 1990 up to >100 in the 2000s. A slight decrease was then observed in the driest years. The extent of P and N loadings and their relationships are key issues for environmental policies aimed at protecting the Adriatic Sea (Vollenweider, 1992), with strong implications for agriculture, livestock and urban wastewater management. De Wit & Bendoricchio (2001) and Palmeri *et al.* (2005) estimated the potential effects of environmental policies on reduction of N and P loadings by 2020, assuming four scenarios: business as usual (BAU), limitation of agricultural and manure surplus, the performance/implementation of urban waste-water treatment plants (WWTP), and a combination of better performances of agriculture and WWTP. As expected, the latter solution gave the best results with reduction of loadings to 4500 (TP) and 59 000 (TN) t $year^{-1}$, demonstrating that the implementation of better practices is a stepping stone for rehabilitating water quality in the Po River. However, one can see that values obtained with simulations of the best scenario were similar to values achieved in dry years, demonstrating that the policy effectiveness is strongly dependent on hydrological conditions.

SHORT-TERM VARIABILITY OF HYDROLOGY, NUTRIENT LOADINGS AND STOICHIOMETRY IN DRY YEARS

The nutrient load formation and delivery from the Po River to the Northern Adriatic Sea was evaluated considering the large and sudden variations of water discharge rates, particularly flash flood events that can occur under altered climatic conditions. The temporal variability of nitrogen and phosphorus loads at the basin's closing section of Pontelagoscuro was studied from 2003 to 2007, specifically considering the contribution of flood events to the total annual load (Naldi *et al.*, 2010). The main nutrient concentrations were determined biweekly during normal water discharge periods ($Q < 1500\ m^3\ s^{-1}$), and every 12–24 hours during flooding events ($Q > 1500\ m^3\ s^{-1}$).

A high frequency of days with average flow rate below the annual average of the period 1961–1990 was observed from 1991 to 2007. Very low discharge flows lasted for about two months in summers 2005 (65 d), 2006 (74 d) and 2007 (66 d), with a discharge of less than $500\ m^3\ s^{-1}$, and especially in 2006 when it was $<250\ m^3\ s^{-1}$ for 43 days. Under these conditions, TP concentrations did not follow a seasonal pattern, but were subjected to sudden and rapid changes accompanying the increase in flow rate (Table 2). In particular, during floods TP and particulate phosphorus (PP) were strongly correlated to total suspended solids. SRP concentrations remained at background levels and were not affected by flow rate variations to any appreciable extent. From 2003 to 2007, nitrate concentrations (>95% DIN) followed a strong seasonality, with summer minima and extremely high winter peaks. Neither significant interannual differences, nor appreciable differences between flood events and normal flow rates were observable for nitrate concentrations (Table 2).

Table 2 Concentrations of SRP, TP and nitrates under normal and flood flows (Naldi *et al.*, 2010).

	SRP ($\mu g\ P\ L^{-1}$)	TP ($\mu g\ P\ L^{-1}$)	NO_3-N ($mg\ N\ L^{-1}$)
Normal flow	56±23	158±63	2.28±0.91
Flood flow	57±23	405±275	2.73±0.83

The temporal evolution of the nitrogen loads did not depend on floods, but was directly related to the total discharge rate. The annual TP loads varied between 5400 to 9300 t $year^{-1}$ and largely depended on flood events. Flood events lasted only for a short time, therefore most of the annual TP load was delivered in just a few weeks, e.g. 29% in 19 days (2006) and 40% in 37 days (2005). Overall, under drought conditions, 20–40% of the annual TP load was released in less than ~10% of the year, thus representing a sort of "flash loading". The speciation of the TP loading was studied with sequential extraction techniques by Giordani *et al.* (2010). A significant fraction of the TP load was composed of insoluble and refractory organic P during floods. Therefore, the increased P availability was only apparent, because most of the particulate P (PP) load was insoluble and not available to primary producers, it being composed mainly by particulate organic refractory and Ca-bound P (Table 3). By contrast, during lower flow periods the exchangeable and Fe-bound P increased, delivering readily available P, but at much lower concentrations. This means that phosphorus may become a limiting factor for primary producers.

Flood events also caused changes in the stoichiometric ratio of nutrients. During ordinary flows, the molar TN:TP varied from 35 to 49, whilst the flood loads had instead a much lower ratio (6–21), close to that of Redfield. The DSi:DIN and DSi:SRP ratios evidenced that there was a potential P limitation (Table 4). The DSi was also imbalanced with respect to DIN, with potential stress for phytoplankton communities. Therefore nitrogen, especially nitrate-nitrogen, became a critical issue for water quality and eutrophication processes. Indeed, the Po River is considered eutrophic**,** based on nutrient and chlorophyll-a concentrations. In particular, chlorophyll-a peaks of up to 70–80 $\mu g\ L^{-1}$ were observed under summer, low-discharge conditions, and autotrophic production was shown to be limited by phosphorus availability during the May–October growing period (Rossetti *et al.*, 2009; Tavernini *et al.*, 2011).

Table 3 Comparison of particulate phosphorus (PP) concentrations and PP speciation under low and flash flood flows. TSS: Total Suspended Solids, POP: particulate organic P, exch-P: reactive P extractable with $MgCl_2$, P~Fe: iron bound P, P~Ca (A): authigenic calcium bound P, P~Ca (D): detrital calcium bound P (see Giordani*et al.*, 2010, for methods and details).

	19 Sept 07	26 Nov 07
Q (m^3 s^{-1})	725	3419
TSS (mg L^{-1})	102	1340
TP (μg P L^{-1})	204	1195
PP (μg P L^{-1})	164	1140
POP (%PP)	53	60
exch-P (%PP)	21	6
P~Fe(%PP)	10	5
P~Ca-A(%PP)	13	22
P~Ca-D(%PP)	3	7

Table 4 Molar DSi:DIN and DSI:SRP ratios of the annual nutrient loads delivered by the Po River to the Adriatic Sea. Data are obtained from Table 1 for DIN and SRP, and from Viaroli *et al.* (2013) for dissolved silica (DSi).

	DIN (t N $year^{-1}$)	SRP (t P $year^{-1}$)	DSi (t Si $year^{-1}$)	DSi:DIN	DSi:SRP
1968-70	53 028	1825	111 707	1.05	67.5
2004	134 301	2512	172 132	0.64	75.6
2005	87 222	1674	101 799	0.58	67.1
2006	77 942	1723	97 393	0.62	62.4
2007	61 434	1542	77 019	0.62	55.1

Short-term and interannual variations of stoichiometric ratios induced by hydrological changes may affect the composition of algal communities in both the river and the adjacent coastal zone. In the marine areathe DIN enrichment may promote the growth of nitrophilous macroalgae (Viaroli *et al.*, 2008), while pulsed SRP excess may stimulate blooms of toxic algae (Billen & Garnier, 2007). Finally, the DSi shortage in riverine waters may result in cascade reactions through the marine food webs (Humborg *et al.*, 1998).

LAND USES AND NITROGEN CONTAMINATION

To date, nitrogen contamination in the Po River basin has had harsh implications for environmental policies. The debate is focused on identifying the main nitrogen sources, with conflicting issues between diffuse sources (agriculture and livestock) and point sources (urban areas and WWTP). The relationships between land uses and potential nitrogen sources were assessed in the watersheds of four tributaries of the Po River (Table 5, Fig. 1). These catchments were selected because they represent typical case studies of lowland exploitation for urban development, agriculture and animal husbandry. These basins differ in population density and livestock, whilst they have similar farmland in the range 58–75% of the total surface. In the most densely populated basins, the urban and point sources of N accounted for <15% of the total input (Soana *et al.*, 2011). The Po di Volano watershed has the lowest livestock density, and consequently has a very low manure disposal in soils. The other watersheds have a high livestock load, especially the Oglio basin, which generates an elevated nitrogen surplus from soils. In the Parma River basin, nitrogen fixation was similar to livestock loading, due to the wide cultivation of alfalfa for fodder. Accordingly, Bartoli *et al.* (2012) estimated for the Oglio River one of the highest fluvial N exports observed in a river outlet. However, these values are in the medium-high range of European catchments generally (Grizzetti *et al.*, 2012). Bartoli *et al.* (2012) have also shown that the intensive land use is responsible not only for nitrate contamination of surface waters, but also that there is a missing N quota which likely accumulates in the groundwater aquifers.

Table 5 Comparison among four different sub-basins of the Po River watershed. Both N loads and uptake are referred to the agricultural surface area. Livestock refers to cattle and swine. The N budget was estimated following Oenema *et al*. (2003).

	Oglio River[a]	Mincio River[b]	Parma River[c]	Po di Volano[d]
Surface area (km^2)	3840	855	789	2631
Agricultural land (%)	58	68	75	70
Inhabitants km^{-2}	333	220	217	134
Livestock units km^{-2}	717	632	107	22
N livestock manure (%)	51	52	42	5
N synthetic fertilizers (%)	34	28	7	67
N crop uptake (%)	39	39	79	55
Average N input (kg N ha^{-1} $year^{-1}$)	450	365	279	214
Average N surplus (kg N ha^{-1} $year^{-1}$)	180	148	162	60

Data sources: (a) Soana *et al*. (2011) and Bartoli *et al*. (2012); (b) Soana *et al*., unpublished; (c) Nizzoli *et al.*, unpublished, (d) Castaldelli *et al*. (2013)

Changes in agriculture, e.g. the substitution of permanent meadows with annual crops, and in husbandry techniques, along with reduced straw return to the soil, can potentially perturb N cycling in soils and waters. These perturbations can be locally exacerbated due to the exponential development of bio-energetic crops, especially maize. Recent and sudden changes in either agricultural and breeding practices or crop typologies have to also be considered as possible perturbations for the Si cycling (Viaroli *et al.*, 2013). Under these circumstances, agronomic practices, along with possible feedback loops between agriculture and livestock, need to be further investigated to assess the present status and future evolution of diffuse pollution.

CONCLUDING REMARKS AND PERSPECTIVES

In the Po River watershed, the increasing frequency of extreme hydrological events can have profound impacts not only on river discharge, water retention capacity and average return periods, but also on the capacity to buffer flood flows and to withstand drought periods.

Another set of implications deals with biogeochemical cycles within the river and across the multiple land–water interfaces. Nowadays, river–floodplain connectivity is a critical issue, because floodplains are no longer connected to the riverbeds. This is causing a shift from wet to dry soils and a dramatic loss of riparian water bodies and wetlands in the floodplain. These ecosystems, which can potentially remove large nitrogen quantities, have almost disappeared in the rivers crossing the farmland (Racchetti *et al.,* 2011). Overall, the loss of floodplain–river connectivity at times of extreme low water discharge in hydraulically altered rivers is expected to further depress the biogeochemical buffering capacity to pollution, in particular N excess.

The smoothed flood pulses are increasingly less frequent and replaced by sudden and fast floods, which hamper biogeochemical buffers in the riverbed and enhance erosion. Furthermore, the degradation of river quality will be exacerbated by soil erosion and runoff, which will likely increase nutrient and contaminant delivery to rivers.

Along with local hydrological alterations, climate changes are foreseen to deeply modify the frequency and intensity of precipitation, with a dramatic decrease of up to ~50% of rainfall in summer and with a potential runoff decrease of between–10 and –40% (Coppola & Giorgi, 2010).

The maintenance of a BAU agriculture in periods of water scarcity will likely induce reactive policy responses, i.e. river impoundments and damming. This is also a key issue for farmer organizations, to counteract drought effects on the most appreciated crops (maize, tomatoes and grass fodder for livestock), which have high water requirements. The huge water demand for agriculture often causes conflicts with other stakeholders, as well as posing serious threats to the maintenance of the minimum vital and ecological flows. There is less awareness of the cascade effects the reduced flows of the Po River may have on the deltaic branches and the Adriatic Sea (Viaroli *et al.*, 2012).

We had the opportunity to test a possible scenario of extremely reduced flows in the summers from 2003 to 2007, when at Q < 250 m^{-3} s^{-1}, the salt wedge expanded 20–25 km upstream in the main branches of the Po Delta (Angonese, 2006). The high salinity in both surface and ground waters severely impaired water use for both irrigation and drinking purposes. Changes in river flow are also expected to have effects on food webs in the transitional and coastal waters, e.g. decreased food availability for filter feeders, molluscs, lowering shellfish farming production (Viaroli *et al.*, 2012). Overall, the extent, duration and frequency of extreme hydrological events can have catastrophic impacts in estuarine, transitional and adjacent coastal marine ecosystems, and also possible regime shifts (Flemer & Champ, 2006).

In the Po River basin, nutrient sources (especially N) are clearly related to soil uses, but nutrient inputs to rivers may also be strongly influenced by hydromorphological alterations and climatic changes. The policies enforced to date have been apparently more effective for reducing P than N loadings, and for controlling point-sources rather than diffuse sources. However, the reduction of loads alone is not sufficient for improving water quality. Speciation and stoichiometry of N, P and Si have to be further examined in relation to their effective availability under changing hydrological conditions, and the nonlinear responses of aquatic food webs have to be considered.

To tackle a warmer and dryer climate, adaption measures have to be implemented in all sectors. First of all, since agriculture alone accounts for 70% of water uses, agricultural practices have to be reorganized with the main goal of saving water, for example with different irrigation techniques and crop typologies, and water and wastewater re-use.

The restoration of river morphology is also a priority and may include rehabilitation of lateral connectivity, restoration of wetlands in the floodplain and riparian buffer zones, re-meandering and re-construction of braided morphology. Along with intervention in the main river and streams, we consider as a key issue the rehabilitation and the ecologically-oriented management of the canal system that drains into the main water courses. The development of the secondary drainage network in the Po Plain dates back 100s of years and most of this “artificial” system is at present strongly integrated into the watershed dynamics. Some areas of the secondary drainage network host a large fraction of macrophyte diversity (Bolpagni *el al*. 2012) and relevant ecosystem services, i.e. nutrient retention or dissipation (Soana *et al.*, 2011; Pierobon *et al.*, 2013). Therefore, the oversimplification of such landscape elements with the only purpose of increasing the hydraulic efficiency of the network sets to zero the economically and ecosystem relevant services. Nearly 50 000 km of major canals and probably twice as much developed ditch networks have a large potential, if correctly managed, to ensure water retention, even at times of water scarcity, to promote the conservation of biodiversity and to enhance nitrate removal, P retention and a balanced control of coupled nutrient cycles.

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