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Nitrogen balance and fate in a heavily impacted watershed (Oglio River, Northern Italy): in quest of the missing sources and sinks

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Abstract

We present data from a comprehensive investigation carried out from 2007 to 2010, focussing on nitrogen pollution in the lower Oglio River basin (3800 km^2, Po plain, Northern Italy). Nitrogen mass balances, computed for the whole basin with 2000 and 2008 data, suggest a large N surplus in this area, over 40 000 t N yr^{-1}, and increasing between 2000 and 2008. Calculations indicate a very large impact of animal husbandry and agricultural activities in this watershed, with livestock manure and synthetic fertilizers contributing 85 % of total N inputs (about 100 000 t N yr^{-1}) and largely exceeding crop uptake and other N losses (about 60 000 t N yr^{-1}). Nitrogen from domestic and industrial origin is estimated as about 5800 and 7200 t N yr^{-1}, respectively, although these loads are overestimated, as denitrification in treatment plants is not considered; nonetheless, they represent a minor term of the N budget. Annual export of nitrogen from the basin, calculated from flow data and water chemistry at the mouth of the Oglio River, is estimated at 13 000 t N yr^{-1}, and represents a relatively small fraction of N inputs and surplus (~ 12 % and 34 %, respectively). After considering N sinks in crop uptake, soil denitrification and volatilization, a large excess remains unaccounted (~ 26 000 t N yr^{-1}) in unknown temporary or permanent N sinks. Nitrogen removal via denitrification was evaluated in the Oglio riverbed with stable isotope techniques ($\delta^{15}N$ and $\delta^{18}O$ in nitrate). The downstream final segment of the river displays an enriched nitrate stable isotope composition but calculations suggest a N removal corresponding to at most 12 % of the unaccounted for N amount. Denitrification was also evaluated in riverine wetlands with the isotope pairing technique. Areal rates are elevated but overall N removal is low (about 1 % of the missing N amount), due to small wetland surfaces and limited lateral connectivity. The secondary drainage channel network has a much higher potential for nitrogen removal via denitrification, due to its great linear development, estimated in over 12 500 km, and its capillary distribution in the watershed. In particular, we estimated a maximum N loss up to 8500 t N yr^{-1}, which represents up to 33 % of the unaccounted for N amount in the basin. Overall, denitrification

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in surface aquatic habitats within this basin can be responsible for the permanent removal of about 12 000 t of N per year; but the fate of some 14 000 t remains unknown. We provide evidences that an important N sink in this basin could be represented by groundwater. In the short term, the aquifers can store nitrogen and available data on nitrate concentration in wells support this hypothesis. In the mid-long term, part of the accumulated nitrate can be substantially recycled via springs and can pollute surface waters via river-groundwater interactions. This probably explains the ten fold increase of nitrate concentration in a reach of the lower Oglio River where no point pollutions sources are present.

1 Introduction

Over the last 50 years, nitrogen cycling in watersheds heavily exploited by agriculture and animal farming has undergone major alterations as a consequence of multiple interplaying factors (Vitousek et al., 1997). Increased manure production and spreading, use of industrially fixed nitrogen fertilizers, fixation by crops and atmospheric deposition have resulted in a release of reactive nitrogen into the environment greatly exceeding crop uptake and other N-removal processes (Puckett, 1995; Cassman, 2002; Galloway et al., 2008). Simultaneously, intensive agricultural practices have simplified the landscape and removed natural buffers as vegetated riparian areas. The absence of these elements has greatly enhanced nitrogen lateral and vertical migration and made the surface and groundwater more prone to nitrogen contamination (Balestrini et al., 2011). This risk is augmented by the use of large water volumes for irrigation and by traditional practices based on soil flooding over permeable areas, that enhance N loss via runoff and leaching (Cassman, 2002; Böhlke et al., 2007). High infiltration rates decrease groundwater residence time, altering rates of biogeochemical reactions; elevated concentrations of nitrogen in surface waters saturate microbial processes and uptake by primary producers, making nitrogen control by natural processes less effective (Böhlke et al., 2007; Mulholland et al., 2008). This increased N loading has a suite of negative

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consequences, including demonstrated health effects, enhanced eutrophication, and contributions to global warming (Ward et al., 2005; Davidson, 2009; Howarth et al., 2011). Open questions about the fate of the nitrogen surplus in impacted watersheds concern where and for how long does the excess nitrogen accumulate, and what processes and transformations does it undergo (Puckett et al., 2011).

We addressed these and related questions in the lower Oglio River, a central sub-basin (3800 km^2) of the Po River watershed, which is the largest river basin in Italy (71 057 km^2). About 50 % of the Po watershed is exploited for agriculture. The Po basin hosts a human population of 17×10^6 inhabitants, approximately 3.1×10^6 cattle (~ 50 % of the national stock) and 6.0×10^6 pigs (~ 65 % of the national stock). Agriculture and livestock together contribute ~ 80 % of the total nitrogen load generated by the Po River basin of 550 000 $t\,N\,yr^{-1}$, which has led to a diffuse nitrate contamination of both surface and groundwater (Cinnirella et al., 2005). Furthermore, the net annual nitrate load from the Po River has increased 2–3-fold over two decades, from ~ $40 \times 10^6\,t\,N\,yr^{-1}$ in the period 1968–72 to $80 \times 10^6\,t\,N\,yr^{-1}$ (dry years) up to $143 \times 10^6\,t\,N\,yr^{-1}$ from 1990 onwards. This delivery of N represents the major N input term in the Adriatic Sea (Franco and Michelato, 1992; Zoppini et al., 1995). Within the Po River watershed, we analyzed the sub-basin of the lower Oglio River, due to its elevated human population and farmed animal densities, maize-oriented intensive agriculture, highly permeable soils, landscape simplification and flood irrigation practices.

Original data and information from multiple recent studies are here presented with the goal of quantifying the N sources, sinks, and major transformations within this watershed. First we provide background on the patterns of NO_3^- export within the Oglio River, followed by a summary of the major input and output terms in the N budget, including an estimate of N removal via denitrification in surface waters within the basin. Finally, we evaluate the role of groundwater as N sink and that of springs as hotspots of N recycling.

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2 The nitrate "anomaly" in the Oglio River

2.1 Watershed description

The lower Oglio River is a regulated watercourse originating from a subalpine lake, Lake Iseo (Fig. 1). The regulation practices optimizes the amount of water that flows through a series of 6 hydroelectric power plants located within the first 22 km of the reach. They maintain lake water level within a narrow range (184.85 to 186.55 m a.s.l.) and retain lake water during non-irrigation periods in order to release more water for agricultural needs during summer. Water release from Lake Iseo is $45 \pm 33\,m^3\,s^{-1}$ during the non-irrigation period and $67 \pm 32\,m^3\,s^{-1}$ (www.laghi.net/Oglio/) during the irrigation period, generally between May and September. During the irrigation period up to $85\,m^3\,s^{-1}$ can be diverted into a series of artificial channels, mostly located along the Oglio's initial 42 km. As a consequence,water flow in the Oglio is generally at its minimum immediately downstream of these diversions.

For more than 75 % of the arable land in the Oglio River basin, irrigation is performed via agricultural land submersion, a traditional practice made possible by both abundant water availability in this area (with unregulated exploitation) and by coarse-textured soils. The Oglio River crosses the Po plain, the largest alluvial basin in Italy, derived mostly from erosion of the Alps during the Quaternary. Soil particle size decreases with increasing distance from the sediment source, from northwest to southeast across the Oglio watershed (Brenna et al., 2004). Accordingly, the permeability of the unconfined aquifer in the gravels and sands of the higher plain greatly exceeds that of the more clay-rich lower plain. The water table depth varies from about 30 m in the northwest to 2–3 m in the southeast (Carcano and Piccin, 2002). The transition between the two areas is marked by numerous permanent outflows, the so-called "springs belt", that runs parallel to the Alps and is crossed by the Oglio River approximately 30 km south of the Lake Iseo. The Oglio River is fed by groundwater along most of its length (Lombardy Region, 2006).

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2.2 Nitrate trends in summer samplings

Starting in 2007 we conducted detailed, seasonal-based monitoring of the Oglio River water, in the framework of a project aimed at defining restoration strategies and the minimum vital flow of this river (Racchetti et al., 2008, 2010). Flow measurements were performed by Oglio Consortium, the Oglio River water management authority. Water samples were collected from about 80 stations along the rivercourse, including riverine sites ($n = \sim 60$), the main tributaries, and point sources such as wastewater treatment plants (WWTPs, $n = 20$, Fig. 1). All samples were analyzed for dissolved and particulate forms of nitrogen (NH_4^+, NO_2^-, NO_3^-, dissolved organic –DON- and particulate –PN-) by means of standard spectrophotometric techniques (A.P.H.A., 1981). In selected campaigns samples were also collected from the Oglio River course and from tributaries for stable isotope ($\delta^{15}N$ and $\delta^{18}O$) analyses of dissolved nitrate (Delconte et al., 2011a,b). Isotope analyses were performed using an ion exchange resin method modified from Silva et al. (2000).

This monitoring data revealed recurrent nitrate trends during summer campaigns over the 4-yr period. In particular, nitrate concentrations displayed a steep, 10-fold increase from about 55 to 550 µM over the relatively short reach between km 25 to km 50 (Fig. 2). This reach contains the section of the Oglio River downstream from the last great diversion for irrigation, and is the portion characterized by low flows (5 to 10 $m^3 s^{-1}$). We calculated that the N-NO_3^- increase is equivalent to an N input to the Oglio River varying between 4000 and 8000 kg N-NO_3^- d^{-1}. However, this reach contains no significant tributaries nor WWTPs, which means that point sources are not responsible for the nitrate load. Ammonium and organic nitrogen concentrations are generally low (< 10 µM) so that coupled ammonification and nitrification cannot be responsible for the measured nitrate increase. We thus hypothesized a generalized problem of diffuse nitrate contamination in this area. To verify this hypothesis we conducted a catchment N inventory, including all the potential N sources and sinks.

3 Nitrogen mass balance in the Oglio River watershed

3.1 The contribution of agriculture and animal farming

A detailed nitrogen mass balance was conducted according to the soil system budget approach (Oenema et al., 2003).

The soil system budget was calculated on an annual basis as the net difference between N inputs that included livestock manure, synthetic fertilizers, atmospheric deposition, biological fixation and wastewater sludge, and N outputs that included crop uptake, ammonia volatilization and denitrification in soils, all within the catchment's agricultural land. Among these terms, rates of ammonia volatilization and denitrification in soils were taken from the literature (Bussink et al., 1998; Asman et al., 1998; Rotz et al., 2004; Hofstra et al., 2005) as no data are available for the investigated area.

N budget calculations were performed at a spatial resolution of individual municipalities (500 to 9000 ha in size) using farming census data, then aggregated to the catchment scale by means of GIS techniques. The overall budget gains robustness from the comprehensive and high-resolution datasets available for this area and the use of site-specific agronomic coefficients (for more details see Soana et al., 2011). Balance calculations were performed for the years 2000 and 2008.

These calculations indicated that in 2000 total N input was about 80 000 t yr^{-1} and that most of such input was due to manure (50 %) and to synthetic fertilizers (35 %). Output terms accounted for about 50 000 t N yr^{-1} and were mostly sustained by crop uptake (65 %). The difference between inputs and outputs indicates an excess of about 30 000 t N yr^{-1}. The N budget estimated for the year 2008 was also positive, with inputs exceeding outputs by about 40 000 t N yr^{-1}. N inputs from livestock manure and synthetic fertilizers increased by approximately 20 % in an almost 10-yr period. For both years, and almost everywhere in the catchment, livestock manure was the biggest N source; the only exceptions were some mountain municipalities with less intensive animal farming (Table 1).

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The comparison between N input and output suggests an elevated N surplus in this watershed, averaging 180 kg N ha^{-1} arable land (AL) yr^{-1} in 2008. The N surplus varies greatly across the basin (Fig. 3).

The most critical zone is the middle plain of the Oglio River, where some municipalities have a N surplus exceeding 400 kg N ha^{-1} AL yr^{-1}. To put this surplus in context, the total amount of manure recommended by the European Community to be spread on arable lands (not N surplus) varies between 170 and 340 kg N ha^{-1} AL yr^{-1}. The comparison of the N mass balance between 2000 and 2008 shows that the situation did not improve over the eight years. This contradicts the indications of the Nitrates Directive (91/976/EEC) specifically aiming at the reduction of NO_3^- pollution is surface and groundwater. On the contrary, the data suggest an even larger surplus in 2008.

The Nitrogen Use Efficiency (NUE) of agroecosystems is defined as the proportion of all N inputs that is removed via the harvest of aboveground material in crops (Liu et al., 2008). In the Oglio River basin, NUE decreased from 0.43 to 0.39 between 2000 and 2008, reflecting an increased risk of N runoff and pollution of aquatic ecosystems.

3.2 Domestic and industrial contributions to N pollution

The lower Oglio River watershed had a population of 1 140 000 in 2000 and 1 270 000 in 2008. Assuming a per capita N production of 12.5 g d^{-1}, the N potential load was 5200 t N yr^{-1} in 2000 and 5800 t N yr^{-1} in 2008, with an increase of 11 %. These loads amount to only about 6 % of the total N input to the lower Oglio basin. About 85 % of the total population is connected to the sewage system, meaning that urban wastewater is almost entirely delivered to WWTPs before being discharged into the Oglio River or into the secondary channels within the basin.

Based on regional inventory (Lombardy Region, 2006), there are over 210 WWTPs in the Oglio River basin having a total permitted capacity of about 1 100 000 inhabitants equivalent (IE). Domestic wastewater management is characterized by a multitude of small facilities: about 53 % of the total number of plants have a capacity up to 2000 IE and only 6 % are larger than 10 000 IE. The effluents of 9 WWTPs, collecting domestic wastes of only 4 % of the total IE within the watershed, are discharged directly into the Oglio River main course. The remaining facilities are scattered within the catchment and their effluents enter the secondary drainage network.

Our calculation of potential N load from urban areas is likely a great overestimate of the true N load discharged into surface water by WWTPs, as we did not estimate denitrification occurring in the treatment plants. This is obviously not true because sewage plants with over half (53 %) of the total permitted capacity in the basin operate denitrification as tertiary treatment, and thus remove a variable fraction of the incoming N load. This means that N loads released by WWTPs are likely even smaller than 6 % of the other total N input terms.

Industrial point source N inputs were estimated considering the number of workers in the different N polluting industrial sectors and their specific N production factors (Pagnotta and Barbiero, 2003). Calculations were performed for 2001, the last year for which national census data on industrial activities are available with municipality resolution (National Statistics Institution, 8th Industrial Census 2001; http://dwcis.istat.it/cis/index.htm). The lower Oglio River basin hosted in 2001 over 1 500 000 industrial equivalent inhabitants and N load potentially generated was about 7200 t N yr^{-1}.

3.3 Point and diffuse N sources in the Oglio River

We calculated the relative contribution of diffuse and point sources of N to nitrate loads in the lower Oglio River by dividing the river into 10 homogeneous reaches where flow and chemical data were available for both the river and its main tributaries. For every reach, we calculated the NO_3^- input from tributaries and the net balance between downstream and upstream loads. NO_3^- input from tributaries was considered as a point source while the difference between the upstream and downstream balance and the sum of point sources was considered to be the diffuse source of pollution. In this simplified calculation we did not consider denitrification nor biological uptake within the river reaches; failure to quantify these processes leads to conservative estimates of diffuse N loads. We then integrated the results for the whole Oglio River (Fig. 4). Our

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calculation suggested a strong seasonality of the nitrate budget associated with different water flow, but the contribution of point sources to the nitrate load never exceeded 35 %.

4 Export of N from the basin

The large dataset of flow and water chemistry data allowed the estimation of the annual flux of nitrogen exported from the Oglio River. The calculation was performed by multiplying monthly dissolved and particulate nitrogen concentrations (NH_4^+, NO_2^-, NO_3^-, dissolved organic –DON- and particulate –PN-) by average monthly water flow at the lower Oglio River origin at the Sarnico dam, and at the river's mouth, and then integrating values to one year. Nitrogen contributions from Lake Iseo were subtracted from outflowing total N loads. Data sources for dissolved and particulate nitrogen concentrations are from the database of the Department of Environmental Sciences of the Parma University for 2007–2010 and the database of the Regional Agency for the Environment (ARPA) for 2000 to 2008 (Racchetti et al., 2008, 2010). Daily flow data were extracted from the database of the Oglio River Consortium (1980–2010, www.laghi.net/Oglio/).

Calculated total nitrogen export from the watershed approached 13 000 t N yr^{-1}, with 90 % as nitrate. Comparing population (333 inhabitants km^{-2}) and N export (2950 kg N-NO_3^- km^{-2}) per unit area for the Oglio River basin relative to other impacted watersheds in the world, the Oglio had among the highest of both population density and N export (Caraco and Cole, 1999; Soana et al., 2011). Nitrogen export can thus be predicted based on population, even if catchment mass balances suggest that fertilizer and farmed animals, not humans, contribute mostly to the excess of nitrogen in this territory (Table 1).

Looking at things from another perspective we can argue that N export from the basin represents about 34 % of the N surplus calculated into the watershed, which means that some 26 000 t N are somehow retained within the basin, by processes still to be identified.

This in turn suggests that there are efficient mechanisms causing a net N loss or retention in the basin. These mechanisms could permanently remove N by dissimilative processes (denitrification) or store and/or transport N in another environmental reservoir (soil, groundwater). Below, we address both of these alternatives.

5 Denitrification in aquatic habitats

5.1 Dissimilative nitrogen loss in wetland habitas: high removal over small surfaces

We have investigated the role of denitrification in shallow aquatic habitats within the Oglio watershed, starting with a comprehensive study on perifluvial wetlands (Racchetti et al., 2011).

Wetlands are rare in the Oglio River basin, totalling only 200 ha, or 0.05 % of the watershed area. Small, relict wetlands are scattered throughout the watershed. For example, for three study reaches (Fig. 5) wetlands – mainly oxbow lakes – occupy less than 5 % of the area within embankment that might be flooded. There is little potential for formation of new perifluvial areas, because arable land covers more than 60 % of the basin surface and because embankments impede the lateral mobility of the Oglio River. Furthermore, perifluvial environments are progressively isolated from the main water body by the evolution of the riverine landscape and by eutrophic conditions and rapid infilling.

We characterized benthic fluxes of inorganic nitrogen and rates of denitrification within these isolated and connected environments. During both winter and summer 2007, we collected intact sediment cores from 12 riverine wetlands (marshes, oxbow lakes and ponds) within the Oglio River watershed (Table 2), of which half were hydraulically connected with the river while the remaining were isolated. The cores were incubated in the dark (Dalsgaard et al., 2000), and denitrification rates were measured adding $^{15}NO_3^-$ to the cores water phase, according to the isotope pairing technique (Nielsen, 1992). This method allows to split total denitrification (D_{TOT}) into denitrification of nitrate diffusing to the anoxic sediment from the water column (D_W) and denitrification of nitrate produced within the sediment due to nitrification (D_N).

All sampled environments were eutrophic to hypertrophic, with fluffy and organic sediments (8–33 % organic matter content as LOI), a shallow water column (depth 0.3 to 1.5 m) and small areal extent (< 1 to < 20 ha). Total denitrification rates ($D_{TOT} = D_W + D_N$) were significantly higher in summer than in winter. Rates measured in river-connected wetlands were up to two orders of magnitude higher than rates measured in isolated wetlands, likely due to extremely elevated nitrate concentrations in the water column and to elevated water temperature in summer in the shallow-water systems (Table 2). However, the addition of increasing amounts of $^{15}NO_3^-$ in the water overlying sediments collected at isolated sites resulted in an immediate stimulation of denitrification rates, suggesting an elevated denitrification potential also for these sediments.

Total denitrification was mostly sustained (60–100 %) by denitrification of water column nitrate (D_W), suggesting strong regulation of the benthic denitrification by nitrate availability. The production of nitrate within surface sediments was generally low, due to limited oxygen penetration in organic sediments; as a consequence, rates of coupled nitrification-denitrification (D_N) were negligible. Benthic denitrification in hydrologically connected wetlands rapidly removed nitrate from the water column, but mineralization of organic nitrogen and regeneration of ammonium partially balanced nitrogen loss via denitrification at both isolated and connected sites, especially during summer (Table 2).

In order to quantify the maximum potential of wetland areas within the Oglio River basin to serve as nitrogen sinks via denitrification, we extrapolated the maximum rates measured experimentally at connected sites to all the surface presently occupied by wetlands in Oglio basin. We calculated a maximum potential N removal in wetlands of 250 t N yr^{-1}, a very small amount compared to that generated within the basin or exported to the Po River. Overall, N loss via benthic denitrification was a minor fraction (< 1 %) of the basin N surplus due to limited extent and hydrological connectivity of these environment within the Oglio River.

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5.2 Nitrogen removal in the Oglio River and in the secondary drainage network

We considered the relevance of denitrification in the Oglio River using a dual isotopic approach for the river itself, its main tributaries and other potential nitrate sources in the watershed during 2009 and 2010 (Delconte et al., 2011a,b). Dual isotopic analyses of nitrate in the environment are a powerful tool to assess the presence of denitrification and quantify its relevance. Denitrification causes the isotopic composition of both δ^{15}N and δ^{18}O in nitrate to increase exponentially as nitrate concentration decreases. Isotopic composition increases for both elements in a roughly 2 : 1 ratio, causing data to plot along a slope of about 0.5 δ^{18}O/δ^{15}N (Fig. 6) (Kendall et al., 2008). We report here results from sampling performed in July 2010, during low-flow conditions, although the observed isotopic pattern for the Oglio River water does not show marked seasonal differences (Delconte et al., 2011a).

The Oglio River can be divided into three distinct sections based on patterns of nitrate concentration (Fig. 2) and isotopic composition (Fig. 6). In the upstream reach (first 15 km), the isotopic composition indicated an origin from atmospheric deposition or a contribution from synthetic fertilizers. Between 15 and 45 km, the isotopic composition indicated an anthropogenic organic matter contribution to stream nitrate. Finally, from km 50 onward, an enrichment in δ^{15}N values was observed, while the δ^{18}O values are rather similar to each other, and samples show no clear distinctive signature of the nitrate origin.

Therefore, in the middle and final reach of the river (empty triangles in Fig. 6), a decrease in concentration and an enriched nitrate isotope composition suggest the presence of denitrification. Nevertheless, no clear trend in the isotopic composition is observed with distance downstream. Assuming an isotopic difference in δ^{15}N of at most +4 ‰, and a fractionation factor of 1.020 (Kendall, 1998), denitrification may account for the removal of at most 20 % of the N load at the Oglio River closing section (Mariotti et al., 1988), corresponding to $\sim$3200 t yr^{-1}. Denitrification in the hyporheic zone of the upstream reaches is probably limited by oxic conditions and low organic carbon in the gravel bottom, but is likely to occur downstream, in the riverbed fine sediments. Denitrification may occur as well in soils and groundwater feeding the river. Indeed, in the southern portion of the watershed denitrification in groundwater is indicated by low nitrate concentrations co-occuring with the presence of dissolved Fe and Mn (ARPA Lombardy, 2009). Unfortunately, the distinction between hyporheic and groundwater denitrification is very difficult to establish, since both processes have similar fractionation factors (Hinkle et al., 2001; Sebilo et al., 2003).

By means of a GIS analysis, the total stream length within the lower Oglio River basin was evaluated in over 12 500 km, 95 % of which constituted by low-order ditches. Due to a lack of direct measurements of denitrification rates in the secondary drainage channels, we estimated theoretical nitrate removal by means of hydrochemical data collected during field surveys over several tributaries and according to the equation proposed by Christensen et al. (1990) (for more details see Soana et al., 2011). We extended the maximum theoretical denitrification rate all over the surface actually occupied by the ditch network (about 6250 ha) in this geographical area. The calculated theoretical N removal is equivalent to 5500 t N, denitrified during the 5-month period when the system is active for irrigation practices. In addition, assuming the highest denitrification rates reported in the literature (Mander et al., 1997), we estimated that further 3000 t N yr^{-1} of the surplus in the catchment can be removed in vegetated buffer strips adjacent to the secondary drainage network (linear extension of about 9500 km).

6 Groundwater: nitrogen sink or source?

Denitrification in the Oglio River, in the secondary drainage channel system and in its riparian area can account for at maximum 3200, 5500 and 3000 t N yr^{-1}, respectively, representing about 45 % of the nitrogen amount which is in excess and not exported out of the Oglio River basin ($\sim$ 26 000 t N yr^{-1}). These values are intended as maximal rates of denitrification. The final fate of at least 14 300 t N yr^{-1} is at present not known, and we speculate whether groundwater can represent a significant N sink in this watershed.

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In the lower Oglio River basin, nitrate distribution in groundwater from the shallow unconfined aquifer is not uniform (Fig. 7). Concentrations near or above the threshold for drinking water standards (50 mg NO_3^- l^{-1} or 11.68 mg N-NO_3^- l^{-1}) are commonly observed in the higher plain portion of the basin. This northern part is particularly vulnerable to diffuse contamination, due to the combined effects of coarse-grained soils, flood-based irrigation practices, and widespread corn cultivation, a crop that requires large N amendments (Figs. 1 and 7). This area also receives a large excess input of animal manure, leading to N excess (Fig. 3) (ERSAF Lombardy, 2009; Soana et al., 2011). The downward migration of this N surplus is also confirmed by nitrate isotope composition, (enriched δ^{15}N and low δ^{18}O), identifying anthropogenic organic matter as the pollution source in this area (Sacchi et al., 2011). By contrast, in the lower plain, nitrate is often absent from groundwater. This absence is not only due to the low permeability of the unsaturated zone or to reduced N input. Isotopic evidences indicates rapid denitrification occurring within the soil and in groundwater (Sacchi et al., 2011), and this is also confirmed by reducing conditions and the occurrence of Mn and Fe in groundwater (ARPA Lombardy, 2009).

We could thus consider groundwater in the northern part of the Oglio watershed as a sink for the excess nitrogen, particularly during the irrigation period (April–September). In this area nitrate concentrations have increased in groundwater over the last decade, even in relatively deep wells (>30 m) (ERSAF Lombardy, 2009). This temporal trend is concurrent with the increase in animal manure spreading.

Although groundwater is likely an N sink in the short-term, especially if compared to the rapid turnover of surface waters, we have evidences in the Oglio watershed of nitrogen transport to the surface water network, particularly in the "springs belt" zone between the northern and southern portion of the catchment. This area also corresponds to the reach where the nitrate increases sharply in the Oglio River (Figs. 2, 3 and 7). It is thus likely that the river is receiving nitrate-rich groundwater in this section, resulting in the observed increase of nitrate concentrations in the river water.

Rapid extraction of large volume of water for irrigation from permeable areas can lead to reduced water residence times in groundwater (Böhlke et al., 2007). This change has multiple implications, such as faster recycling of pollutants (as nitrogen but also herbicides) and reduced transformation by biogeochemical processes.

Confirmation of this accelerated water recycling is obtained by stable isotope analyses of the water molecule and of dissolved nitrate. In July 2010, in the upper part of the watershed we collected three groundwater samples characterized by high nitrate concentrations. Their isotopic composition is consistent with other groundwater data from the northern part of the basin (Sacchi et al., 2009, 2011) and is similar to that measured in the Oglio River water in that part of the watershed (Fig. 6). Therefore both concentration trends and nitrate isotope composition suggest the presence of mixing between Oglio River and groundwater. In order to validate this assumption, we calculated the amount of groundwater input to the river using the $\delta^{18}O$ values of water molecule. According to this calculation, during summer, the contribution of groundwater to the Oglio River could account for about 60–70 % of the total flow in the portion of the upper course where springs and natural outflows are present and where the nitrate increase occurs. Using this value, we recalculated both the nitrate content and the $\delta^{15}N$ of river water samples and compared them with the measured values. Calculated nitrate concentrations are in reasonable agreement with the measured values. On the other hand, the $\delta^{15}N$ values measured in samples are generally slightly higher than theoretical values, suggesting a minor contribution from other nitrate sources (e.g. WWTPs) or the presence of nitrate that has been recycled in the environment (Wexler et al., 2011; Delconte et al., 2011b).

7 Linking ground and surface water: the springs belt

During 2010 and 2011 water samples were collected from a number of springs and characterized for flow and concentration of dissolved gas and nutrients, in particular O_2, CO_2, CH_4, N_2O, NH_4^+, NO_2^- and NO_3^- (Laini et al., 2011). Water from the springs was generally supersaturated with N_2O and displayed extremely high N-NO_3^-

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concentrations, up to 1400 µM. Overall, within the analyzed watershed, about 50 springs were censused (Fig. 7); each had a relatively low water flow, generally below $50\,\mathrm{l\,s^{-1}}$. They probably represent a small fraction of the deep water that is recycled to the surface, as most of flow occurs not in channels but within the upper soil layers. Deep water movements can mobilize in the mid to long term the pollutants that were stored in groundwater. On the other hand, groundwater mass balance calculations in the area indicate that the water volume outflowing from springs is up to ten times larger than that feeding the Oglio River, suggesting that the "springs belt" represents one of the main discharge areas of the shallow aquifer (Lombardy Region, 2006).

We thus speculate that the nitrate anomaly could be attributed to interactions between the Oglio River water and the shallow aquifer that is particularly rich in nitrate. Such interaction was estimated to be between 4 to $8\,\mathrm{t\,N\,d^{-1}}$ recycled from unconfined groundwater in the 25 km long reach characterized by the nitrate anomaly (Fig. 2). The steep increase of nitrate concentrations in the river water is particularly evident in summer months due to relatively low river water flow.

If our speculation is correct, groundwater serves as a N sink in the short term, but acts as a N source in longer periods of time (> 20 yr), indicating that pollution mitigation measures will not lead to immediate results. This observation is in general agreement with the performance evaluation of the Nitrates Directive application, indicating longer recovery time and less performing results for groundwater with respect to surface water (EEA, 2010). This time lag is generally not appreciated by stakeholders.

8 Discussion and conclusion

In the lower Oglio River basin, most municipalities have a high population of farmed animals, without sufficient agricultural land for manure spreading. The current legislation specifies upper limits on manure spreading of 170 and $340\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$, for vulnerable and non-vulnerable soils, respectively. The arable land area theoretically necessary to spread manure produced in the region should be 3 times higher than

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exists. We demonstrated that excessive manure spreading has led to a large anthropogenic excess of bioavailable nitrogen to the watershed and to broad-scale diffuse contamination by nitrate. We found elevated concentrations of N-NO_3^- in the Oglio River, in most of its tributaries, in all wetlands hydraulically connected with the river and in groundwater. High concentrations of N-NO_3^- in all water compartments is an evident sign of N-saturation in the terrestrial but probably also in the aquatic portions of the watershed (Mullholand et al., 2008). Available information suggests that the contamination of groundwater is an ongoing process, as nitrate concentrations keep increasing (ERSAF Lombardy, 2009) even if at present no informations are available on when such N was added to the basin. Nitrogen budgets for other large watersheds show that an average of about 75–80 % of the nitrogen input is retained within the watershed, suggesting the presence of large N sinks (e.g., Howarth et al., 1996). We calculated that the per km^2 nitrate export of the lower Oglio River is among the highest in the reported literature (Caraco and Cole, 1999; Howarth et al., 2011). Simultaneously, the fraction of N exported from the lower Oglio watershed is only 14 % of the nitrogen added, meaning that large N sinks exist also in this basin. Such outcome should be carefully considered, as the main N-sink function within the watershed is likely contributed by processes that result in net N-accumulation in the watershed and not by dissimilative processes that promote a permanent nitrogen loss. Such accumulation can result in nitrate contamination of groundwater, but also in organic N enrichment within arable lands or particulate N burial in aquatic environments, the latter two not considered in the present study. Our measurements suggest that wetlands have the potential to remove, per unit area, large amounts of N. Denitrification rates measured at connected sites for example were among the highest reported in the literature, up to 1800 µmol N m^{-2} h^{-1} (Seitzinger et al., 2006; Piña-Ochoa and Álvarez-Cobelas, 2006). Nevetheless, when integrated over the catchment's total wetland areas, annual rates of denitrification in wetlands appear to be insignificant sinks, due large N excess and the small surface occupied by wetlands. Our results support the importance of restoring lateral interactions between the river and its perifluvial areas, as we have found

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elevated denitrification potentials also at isolated sites. These latter sites tend to have lower oxygen concentrations in the water column, elevated respiration rates and elevated nitrogen recycling to the water column, resulting in low denitrification efficiencies (Table 2; Eyre and Ferguson, 2002).

Nitrate isotope analyses, together with N mass balance calculations in the lower Oglio River, also suggest that denitrification in the Oglio River itself is probably a minor N sink. The lateral interactions with the surronding areas are in fact extremely limited in time and in space due to the regulation of water flow and the presence of banks for most of its course. The secondary drainage network is capillary extended in this watershed and accounts for 100 times the length of the river, with proportionally more interfaces for microbial processes to occur. The secondary drainage network may be an important sink for bioavailable nitrogen owing to its hydrological connections with terrestrial systems, high rates of biological activity, and streambed sediment environments that favour microbial denitrification. Still, our estimates suggest that nitrogen removal via denitrification in irrigation channels is at maximum 45 % of the missing nitrogen amount.

Nitrogen accumulation in groundwater can be a large potential sink for N, but is short term. There is little information dealing with the turnover of nitrogen in groundwater. In the long term such N could be substantially recycled to the surface and act as an internal source of pollution, with strong analogies with organic sediments in eutrophic lakes (Puckett et al., 2011). Even if allochtonous sources of pollution are controlled, lakes can remain eutrophic for many years as nutrient recycling sustains primary productivity. The nitrate anomaly in the Oglio River is due to an interaction between the Oglio River and nitrate rich groundwater, with an estimated nitrogen input from groundwater varying between 4 and 8 t per day. This flux is only the groundwater that is recycled to the river, but groundwater can analogously interact with other surface aquatic bodies within the watershed.

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Detailed investigation by hydrogeologists is needed, in order to clarify the path of deep and surface groundwater and to date the nitrogen that is recycled by springs. This will allow for an estimation of the time required by groundwater to recover from nitrate pollution if N loads are significantly reduced in the future.

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Table 1. Nitrogen balance in the lower Oglio River basin computed for the years 2000 and 2008. Data are expressed as tons of nitrogen produced or consumed per year in the whole basin or as kilograms of nitrogen produced or consumed per year per hectare of arable land (AL).

N balance terms	2000		2008	
INPUT	$t\,N\,yr^{-1}$	$kg\,N\,ha^{-1}\,AL\,yr^{-1}$	$t\,N\,yr^{-1}$	$kg\,N\,ha^{-1}\,AL\,yr^{-1}$
Livestock manure	42 521	187	51 512	232
Synthetic fertilizers	27 640	121	33 564	151
Biological fixation	7975	27	12 182	35
Atmospheric deposition	1800	8	1800	8
Wastewater sludge	–	–	1057	5
$\sum$ input	79 936	351	100 115	450
OUTPUT				
Crop uptake	34 259	150	38 915	175
NH_3 volatilization	10 147	45	12 704	57
Denitrification in soils	7016	31	8440	38
$\sum$ output	51 422	226	60 060	270
Balance	28 514	125	40 056	180

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Table 2. In situ nitrate concentration and temperature, ammonium and nitrate plus nitrite fluxes, denitrification rates and denitrification efficiency measured in 12 riverine wetlands during summer and winter 2007. Half of the study sites were connected with (C) and half were isolated (I) from the Oglio River. Denitrification efficiency was calculated as the ratio between denitrification rates and inorganic nitrogen effluxes (DIN+N_2) across the sediment-water interface (Eyre and Ferguson, 2002) and as the ratio between denitrification and the theoretical ammonium production within sediments (A) (Dalsgaard, 2003).

		Winter		Summer	
		I	C	I	C
In situ	T (°C)	10.20 ± 1.02	9.33 ± 0.61	25.20 ± 0.20	24.50 ± 0.56
	NO_3^- (µM)	23.00 ± 14.38	677.17 ± 124.06	26.80 ± 21.64	590.33 ± 94.38
Fluxes	NO_X^- (µmol m^{-2} h^{-1})	−30.62 ± 84.69	−630.75 ± 313.98	−109.97 ± 47.68	−1180.68 ± 817.66
	NH_4^+ (µmol m^{-2} h^{-1})	187.49 ± 219.35	−17.71 ± 38.40	367.91 ± 124.06	499.46 ± 464.25
Denitrification	D_W (µmol m^{-2} h^{-1})	49.50 ± 15.44	148.08 ± 35.97	64.44 ± 35.00	651.38 ± 256.26
	D_N (µmol m^{-2} h^{-1})	2.77 ± 2.76	32.50 ± 14.55	17.38 ± 8.90	41.34 ± 22.62
	D_{TOT} (µmol m^{-2} h^{-1})	52.28 ± 13.95	180.58 ± 45.59	81.82 ± 40.93	692.73 ± 244.99
Denitrification efficiency	$D_{TOT}/(D_{TOT} + \mathrm{DIN})$	0.12 ± 0.03	0.44 ± 0.17	0.2 ± 0.07	0.52 ± 0.10
	D_{TOT}/A	0.58 ± 0.22	4.43 ± 0.99	0.48 ± 0.29	6.75 ± 1.43

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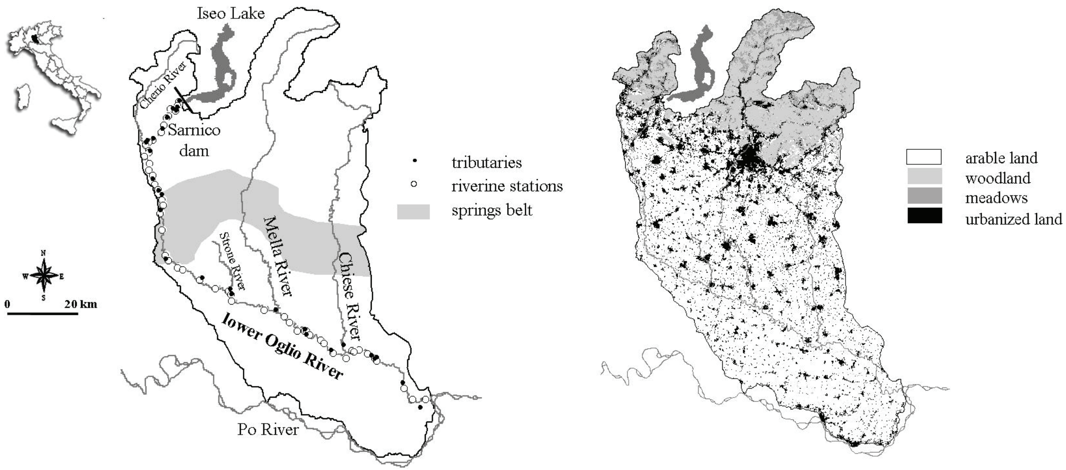

Fig. 1. The two maps show the lower Oglio River watershed with the sampling stations in the river and in its tributaries and the area where springs are situated (left) and the land use (right).

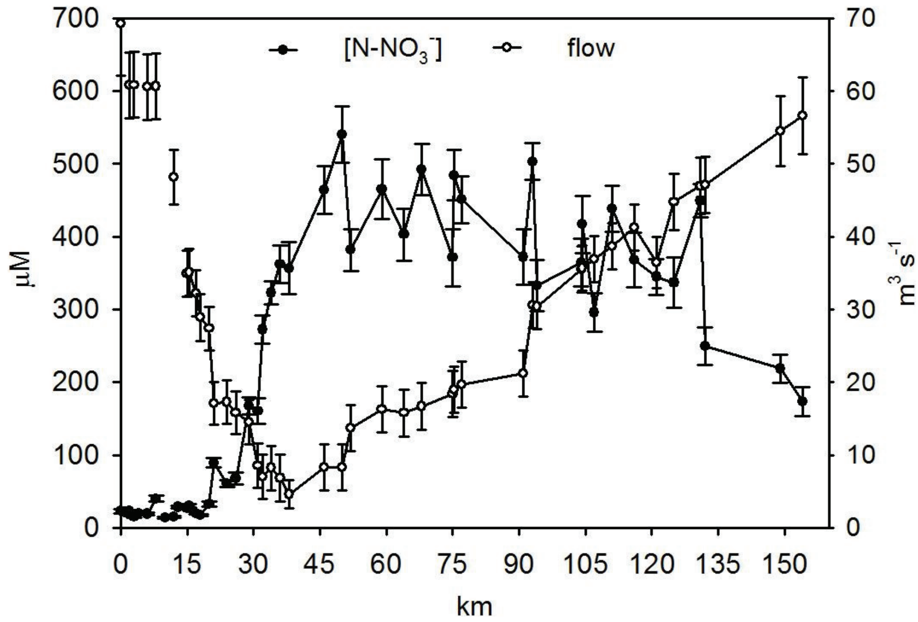

Fig. 2. Concentration of nitric nitrogen and water flow in the lower Oglio River. Values are averages (± standard deviation) from whole river samplings carried out on 3–5 July 2007, 9–11 July 2008, 5–7 August 2009 and 28–30 July 2010.

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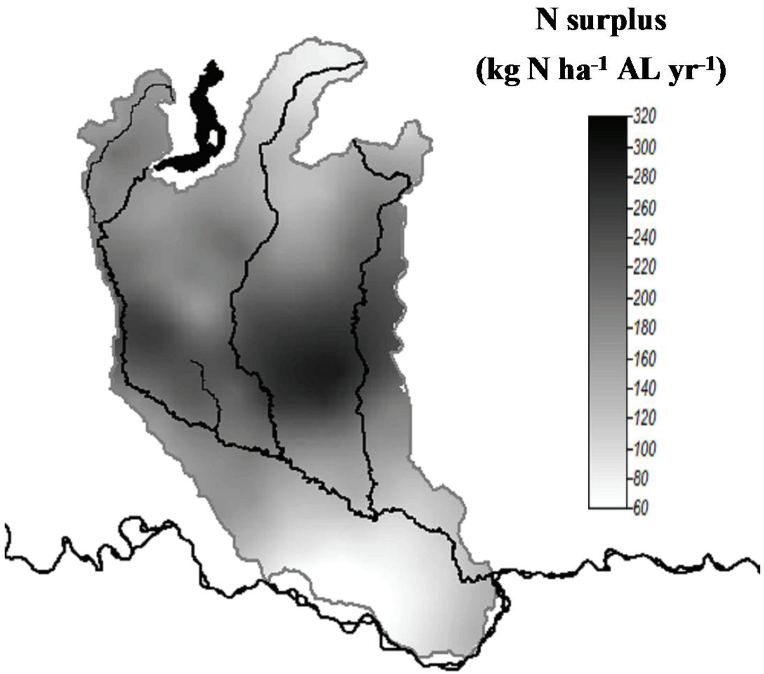

Fig. 3. Spatial distribution of N surplus (= difference between N input and N output terms in a soil system budget) within the lower Oglio River watershed. Values of the N surplus were assigned to the centroid of all the 250 municipalities within the basin and then interpolated by means of the ordinary kriging technique. Calculations were performed with the GIS software SAGA (System for Automated Geoscientific Analyses, version 2.0.5, http://www.saga-gis.org). Data refers to budget calculations of 2008.

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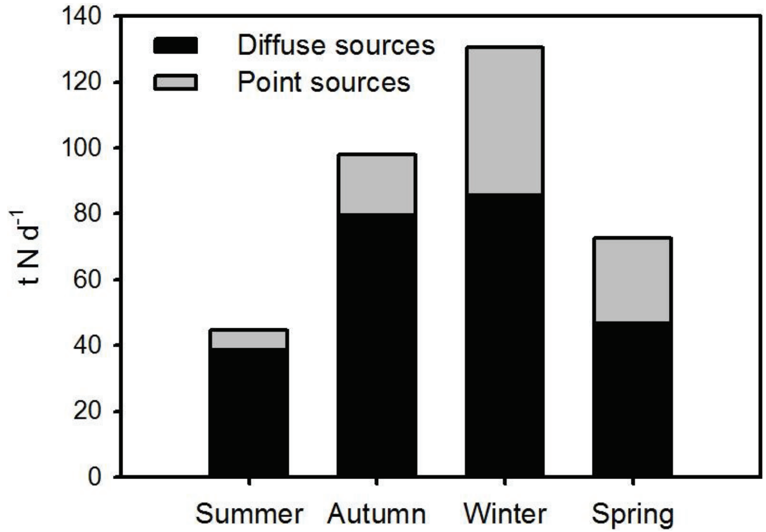

Fig. 4. Diffuse and point sources to nitrate loads in the lower Oglio River.

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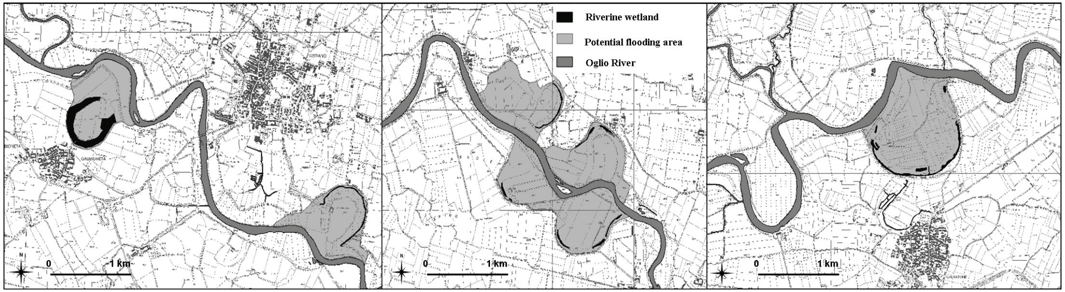

Fig. 5. Examples of relict wetland habitats within the lower Oglio River watershed. These oxbow lakes have a surface varying between 0.60 and 8.28 ha, which is small compared to the area that can be potentially flooded by the Oglio River (from 44.06 to 95.87 ha).

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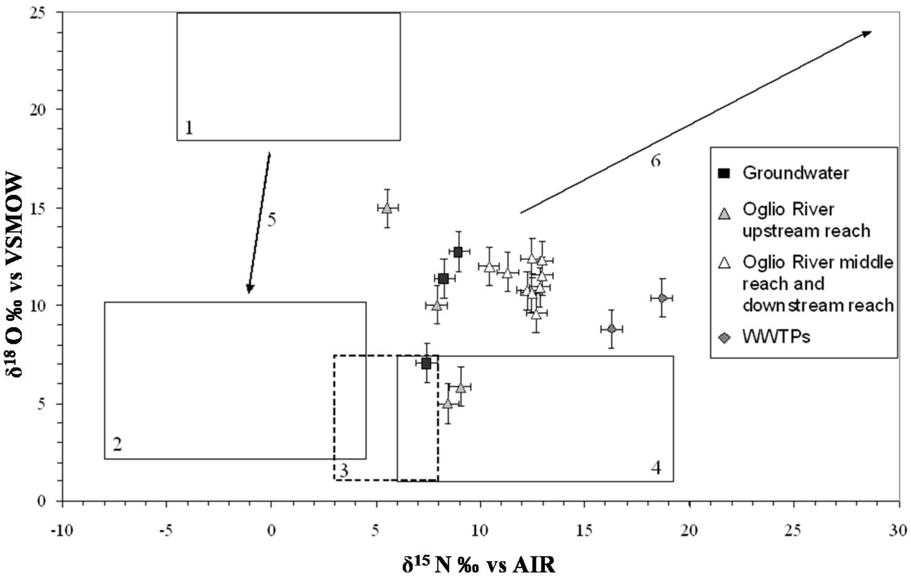

Fig. 6. Isotopic composition of nitrate in water from the Oglio River (full triangles = upstream reach; empty triangles = middle and downstream reach), groundwater (squares) and selected WWTPs (diamonds). Compositional fields: 1 – Synthetic fertilizers; 2 – Mineralized synthetic fertilizers; 3 – Soil organic matter and contamination from mixed sources; 4 – Anthropogenic organic matter (sewage and manure); 5 – Evolution during nitrification; 6 – Evolution during denitrification. Modified after Kendall (1998), and Clark and Fritz (1997).

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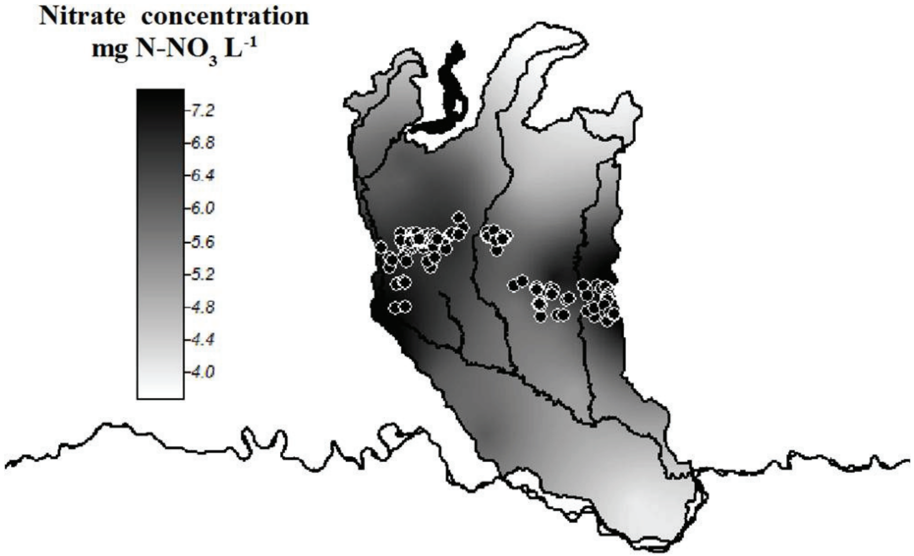

Fig. 7. Mean nitrate concentrations in the surficial aquifer within the ower Oglio River basin (mg $N\text{-}NO_3^-$ l^{-1}, data from 2002–2008). Black dots show the location of censed springs within the watershed and highlight the location of the springs belt, which is at the interface between high and middle plain.

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