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ORIGINAL ARTICLE

Application of QUAL2Kw to the Oglio River (Northern Italy) to assess diffuse N pollution via river-groundwater interaction

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ABSTRACT

Water quality modeling is increasingly recognized as a useful tool for obtaining valuable information for optimal water quality management. In this study, the free software QUAL2Kw was used to evaluate the impacts of agricultural nitrogen (N) excess on river nitrate (NO_3-N) concentrations. We explored the possibility to use QUAL2Kw in order to back calculate the exchange of water and N from the groundwater to the Oglio River, northern Italy, which drains a heavily irrigated and fertilized agricultural land. Along the river course water monitoring activities carried out in the dry, summer period revealed steep increases of NO_3-N in different sectors, by up to 2 orders of magnitude, not explained by any significant point inputs. Such increases suggest the occurrence of large water exchange with nitrate-polluted groundwater and diffuse inputs. In turn, groundwater pollution is due to high N excess in the watershed (~200 kg N ha^{-1} yr^{-1}), flood-based irrigation techniques and soil permeability. The QUAL2Kw model was calibrated using the average of 2 years' data collected in winter 2010 and 2011 and validated using the data of winter 2012. To minimize the error between simulation results and measured data, the constants of inorganic suspended solid (ISS), ammonium (NH_4-N), nitrate and organic N were calibrated. The calibration and validation results showed a good correspondence between the calculated and measured values for most of water-quality variables. QUAL2Kw was then run separately with three years' summer data (2009, 2010 and 2011), and large gaps were found between the measured and predicted values of discharge, electrical conductivity, NO_3-N and total N. Such gaps are discussed in terms of river-groundwater interactions, limited to the summer period and following irrigation by flooding, rise of the groundwater table and vertical transport of N. The gaps allowed to back calculate the volumes of water and the amount of N exchanged. The total load of NO_3-N entering into the river from groundwater was estimated in 25.17, 25.63 and 29.89 ton per day for NO_3-N in 2009, 2010 and 2011, respectively. Similar results were obtained in another study based on mass balance of N isotopes. The combination of experimental and QUAL2Kw modelled data proved to be a simple, low cost but effective tool in the estimation of NO_3-N exchange between the surface and groundwater.

Key words: QUAL2Kw; river; groundwater; nitrate; irrigation; diffuse pollution.

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INTRODUCTION

Agricultural lands worldwide suffer from excess nitrogen (N) application, resulting in large amounts of N that are not assimilated by crops and may pollute surface and groundwater (Hu *et al.,* 2010; Bartoli *et al.,* 2012). In irrigated areas the high solubility of excess nitrate (NO_3-N) results in large vertical and horizontal flows and fast transfer towards waterbodies (Hu *et al.,* 2010; Sutton *et al.,* 2011; Savci, 2012). Areas with permeable soils and irrigated by flooding undergo major risk of groundwater pollution, with increasing NO_3-N levels and high transfer to surface water (Hu *et al.,* 2010). The latter mechanism is likely explained by vertical migration of aquifers during summer period following irrigation, combined with river-groundwater interactions. This is an example of diffuse N pollution which is extremely difficult to quantify if not by means of multiple measurements of conservative and non-conservative parameters, use of multiple isotopes (^{15}N, ^{18}O, ^{2}Sr, ^{11}B) and mass balances (Bartoli *et al.* , 2012; Delconte *et al.,* 2014).

Even though the continuous monitoring of the water quality and the impact of agriculture on river systems is possible, this approach would be very costly (Wang *et al.*, 2013) and complex (Sophocleous, 2002). To understand these interactions in relation to climate, landform, geology, and biotic factors, a sound hydrogeoecological framework is needed (Sophocleous, 2002). In this regard, water quality modeling is increasingly recognized as a useful tool for obtaining valuable information for optimal water quality management (Cho *et al.,* 2004; Fan *et al.,* 2009; Hadgu *et al.,* 2014; Loucks and van Beek, 2017) and estimating the amount of contamination from point and non-point sources (Gikas, 2014). As compared to the past, complex models for simulation of water quality will be more and more employed in the future due to accumulating data from biological, chemical and hydrogeological disciplines.

In different studies some models were used to evaluate temporal and spatial distribution of water availability including groundwater recharge and quality (non-point NO_3-N loadings). These include SWAT–MODFLOW–MT3DMS (Narula and Gosain, 2013), PATRICAL (Pérez-Martín *et al.,* 2014), and QUAL2Kw models (Gikas, 2014).

QUAL2Kw is a basic, one-dimensional and steady flow stream water quality model with several successful examples of application reported in the literature (Cho *et al.*, 2004; Pelletier *et al.*, 2006; Hassanin, 2007; Kannel *et al.*, 2007; Fan *et al.*, 2009; Allam *et al.*, 2015). QUAL2Kw can simulate a number of constituents including the hydraulic characteristics (discharge and velocity) and water quality parameters (temperature, pH, organic nitrogen, ammonia nitrogen, nitrite and total N) (Kannel *et al.,* 2007). Kannel *et al.* (2007) applied the model for Bagmati River (Nepal) and the model represented the field data relatively well. Zhang *et al.* (2012) reported that the QUAL2K model is a useful tool for the general assessment of water quality improvement programs, and is able to provide decision-making support for the design, implementation and management of river improvement projects. Gikas (2014) demonstrated that QUAL2Kw is a useful tool to simulate water quality in rivers and canals, and to quantify the impacts of non-point source pollution from agricultural areas. Allam *et al.* (2015) used QUAL2Kw to simulate drainage water quantity and quality of the Gharbia drain. Rehana and Mujumdar (2011) used QUAL2Kw to investigate the effect of climate change on water quality.

In this work we explored the possibility to use QUAL2Kw in order to back calculate the exchange of water and N from the groundwater to the Oglio River, northern Italy, which drains a heavily irrigated and fertilized agricultural land. In this river, most water discharge is diverted for irrigation purposes and segments with minimum flows display sudden, marked increases of NO_3-N concentration. Such phenomena were interpreted on the basis of large N excess in the watershed, large vertical transfer of N to groundwater and then back to the river during summer (Bartoli *et al.*, 2012). Our approach is based on the comparison of experimental (including discharge and water chemistry) and QUAL2Kw modelled data. QUAL2Kw was calibrated with winter data, when river-groundwater interactions are close to be null, and run for winter and summer. The good fitting between experimental and modelled data for the winter supported the good calibration of the model, while the gaps between summer experimental and modelled data were used to back calculate river-groundwater interactions.

METHODS

Study area

The Oglio River is a left-side tributary of the Po River located in Lombardy, Italy. Its total length is 280 Km and includes two segments of similar length upstream and downstream the Iseo Lake. In this study we focus on the downstream segment, the “lower Oglio River” with a length of 154 Km, originating from the lake, at Sarnico, and discharging in the Po River at Torre d’Oglio, in the province of Mantua. Fig. 1a shows the lower Oglio River basin, the location of the river course, its main tributaries and the spring belt area. Along its course the lower Oglio River crosses a heterogeneous aquifer system (Bonomi *et al.*, 2014) which is characterized by prevailing high-permeability (hydraulic conductivity in the order of 10^{-3} m/s; Taviani *et al.*, 2017) gravels and sands upgradient, and low-permeability (hydraulic conductivity up to 10^{-8} -10^{-7} m/s; Taviani *et al.*, 2017) silts and clays downgradient. The sharp decrease in permeability along the groundwater flow lines causes the groundwater to partially flow out along the springs belt (Fig. 1b), as shown by the only groundwater flownet available in the scientific literature (Vassena *et al.*, 2008). The Oglio river is fed by groundwater along the downstream portion (from Km 20-30 onwards), while it is usually losing along the upstream one (Km 0-20; Taviani *et al.*, 2017). The variation in terms of hydraulic gradient between river and groundwater observed by Vassena *et al.* (2008) agrees with the permeability distribution and with the highest gradient detected where the river crosses the lower permeability sediments. The altitude of the basin area varies from 13.6 to 181 m above mean sea level. The basin of the lower Oglio River includes a heavily exploited area for animal farming (pigs and cows, for a total of 2,800,000 units) and maize-based agriculture (43% of the cultivated surface). Nearly 2000 Km^2 of agricultural land, extended over more than 58% of the total surface, is heavily irrigated through to a secondary canal network with a linear extension of about 12,500 km (Fig. 1c, Soana *et al.*, 2011). The dominant irrigation technique (66%) is by flooding, due to the large water availability in this area. Most of the water used for irrigation (750 $x10^6$ m^3y^{-1}) is diverted from the river, while only 8% is withdrawn by wells (source: National Institute of Statistics 2010, available at: http://www.istat.it/it/censimento-agricoltura/agricoltura-2010). The mean annual precipitation is about 853 mm y^{-1} (Hijmans *et al.*, 2005; Gardi *et al.*, 2011) and during summer the driver that determines the N dynamic in the watershed is the volume used for the irrigation rather than volume from the precipitation process.

In the river sector crossing the spring belt (Burrato *et al.*, 2003; Vassena *et al.*, 2012) a sudden increase of NO_3-N is documented in the summer, coinciding with minimum discharge and replacement of river water, diverted for irrigation, with NO_3-N rich groundwater from springs (Fig. 1d; Laini *et al.*, 2011; Bartoli *et al.*, 2012). The piezometric map reported in Fig. 1b suggests that during summer the water table rises and groundwater emerges from all springs. As reported in De Luca *et al.* (2014) springs represent a sort of natural piezometric maps.

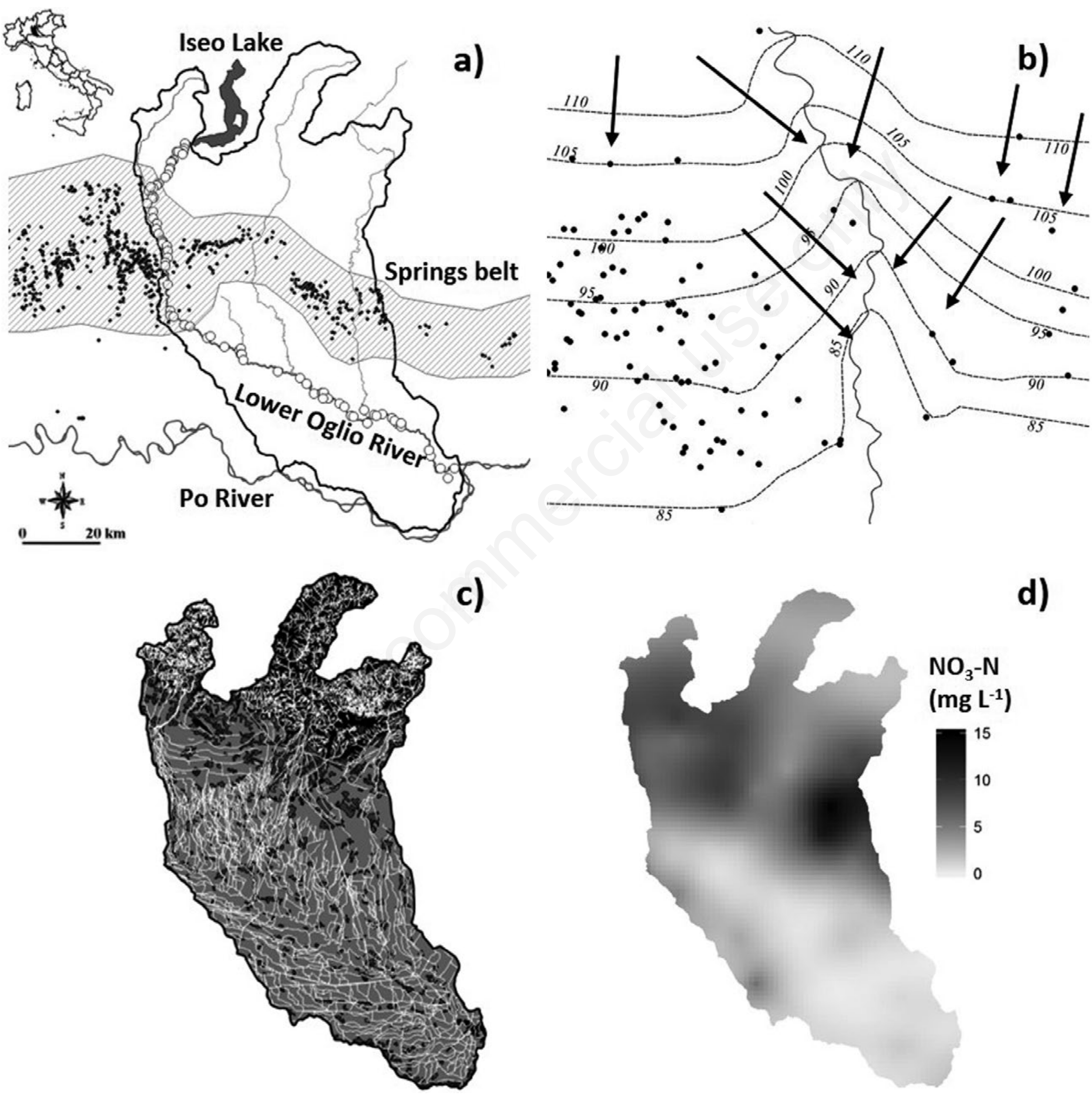

Fig. 1. Location and features relevant to this study of the lower Oglio River basin, Northern Italy. a) Location of sampling stations (white dots), main tributaries and springs (black dots). b) Oglio River course from km 27 to km 37 crossed by springs with indicated piezometric levels (dotted lines) and groundwater flow direction (black arrows) in summer period according to Taviani *et al*. (2017; doi: http://dx.doi.org/10.13125/flowpath2017/2885). c) Land use of the basin from Corine Land Cover 2012: agricultural land (grey), artificial area (dark grey), natural area (black) and river and canals network (white). d) Average NO_3-N concentration (2001-2010) measured in wells monitored by ARPA (Regional Agency for Environmental Protection).

Experimental data and monitoring sites

The lower Oglio River and its tributaries were sampled seasonally from summer 2009 to spring 2012 (n=12) for a total of 100 stations (47 riverine sites, 25 tributaries stations, 22 irrigation channels and 6 hydroelectric power plant sites, Figs. 1 and 2). Most water abstraction structures are located within the upper 40 km of the Oglio River, feeding an extensive network of irrigation canals (Fig. 1c) and 6 hydroelectric power plants. Such comprehensive sampling plan was performed in order to: i) produce an accurate inventory of all point pollution sources; ii) produce a nutrient and surface water budget; iii) compare such budget with differences between upstream and downstream loads/discharge; and iv) address unaccounted for nutrient and water inputs to diffuse pollution, including river-groundwater interactions. Water samples were collected in triplicate at each sampling site from the central part of the river/tributaries/canals by 1 L plastic bottles. Temperature (T) and electrical conductivity (EC) were measured in situ with a multiple probe (YSI model 556 MPS). Water samples were filtered in situ through Whatman GF/F glass fiber filters (porosity 0.45 µm) and transferred to plastic vials for ammonium (NH_4-N), NO_3-N, organic N, total dissolved nitrogen (TN) determinations. Samples were cooled and brought to the lab within a few hours; they were frozen and analyzed within one week with standard spectrophotometric techniques and via ion-chromatography

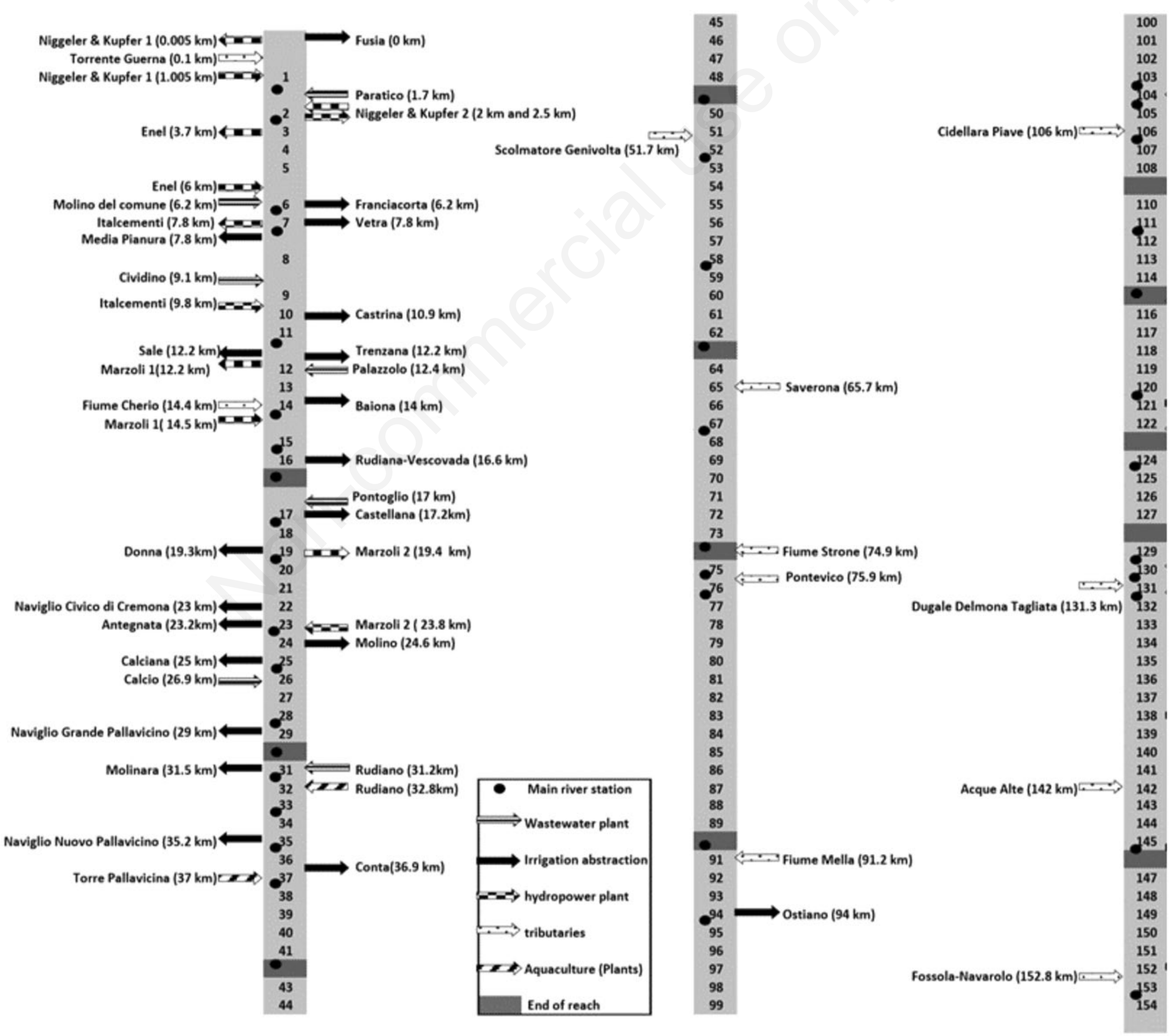

Fig. 2. Modeling segmentation, main river stations, point sources (tributary and wastewater), irrigation abstraction and hydro power plant station locations in the Oglio River.

(APHA, 1996). In the same monitoring stations, the Oglio Consortium performed discharge measurements by means of Rio Grande ADCP (Acoustic Doppler Current Profiler).

Modeling tool

The QUAL2Kw was chosen for the present study because of its popularity and comfort of application. QUAL2Kw has a mass balance equation for a constituent concentration c_i in a reach i as follows (Chapra and Pelletier, 2003).

$$\frac{dc_i}{dt} = \frac{Q_{i-1}}{V_i} c_{i-1} - \frac{Q_i}{V_i} c_i - \frac{Q_{ab;i}}{V_i} c_i + \frac{E'_{i-1}}{V_i}(c_{i-1} - c_i) + \frac{E'_i}{V_i}(c_{i+1} - c_i) + \frac{W_i}{V_i} + S_i \qquad \text{(eq. 1)}$$

where c_i is the concentration of different dissolved or particulate water constituents in reach i (mg L^{-1}) and t is time (s). Q_i and Q_{i-1} are flow rates at reach i and at upstream reach (m^3 s^{-1}), respectively. V_i is the volume of reach i (m^3). E_{i-1} and E_i are bulk dispersion coefficients between reaches i−1 and i and i and i+1 (m^3 s^{-1}). $Q_{ab,i}$ is the abstraction flow at reach i (m^3 s^{-1}). W_i is the external loading of the constituent to reach i (mg s^{-1}). S_i are sources and sinks of the constituent due to reactions and mass transfer mechanisms (mg $m^{-3}s^{-1}$). The model uses a genetic algorithm (GA) to maximize the goodness of fit of the model results compared with measured data by adjusting a large number of parameters. Fitness is determined as the reciprocal of the weighted average of the normalized root mean squared error (RMSE) of the difference between the model predictions and the measured data for water quality constituents. The GA maximizes the fitness function f (x) as follows:

$$f(x) = [\sum_{i=1}^{n} w_i][\sum_{i=1}^{n} \frac{1}{w_i} \left[\frac{(\sum_{j=1}^{m} O_{i;j}/m)}{\sqrt{[\sum_{j=1}^{m} (P_{i;j} - O_{i;j})^2/m]}} \right]] \qquad \text{(eq. 2)}$$

Where w_i, n and m are weighting factors, the number of different state variables (*e.g.* NO_3-N, NH_4-N, organic N and discharge) and the number of pairs of predicted and measured values, respectively. The weighting factor was the same and equal to one for all the considered state variables. $O_{i,j}$ and $P_{i,j}$ are measured and predicted values, respectively. A detailed description of the auto calibration method can be found in Chapra and Pelletier (2003).

Several hourly meteorological data sets have been collected to run the model, including: temperature, wind velocity, solar radiation and dew point temperature at 5 stations of the Oglio River catchment, provided by ARPA Lombardy (Regional Agency for Environmental Protection; available from: http://www.arpalombardia.it/siti/arpalombardia/meteo/richiesta-dati-misurati/Pagine/RichiestaDatiMisurati.aspx) from 2009 to 2012.

The lower Oglio River was divided into 13 reaches with various lengths. The main criterion of this division was the likeness of hydraulic characteristics along a river reach, such as the slope and width, and the similarity of chemical-physical water features. The measured geometries were used to determine the hydraulic characteristics at the end of each reach. Manning's equation was used to determine hydraulic characteristics, water velocity, and depth of the stream. Manning roughness coefficient of 0.03-0.05 was used for all reaches. The boundary conditions at the upstream and downstream extremes were the discharge and the concentration of NO_3-N, NH_4-N, organic N, TN, T and EC (Tab. 1).

Implementation of the model

Winter data used for calibration are the average of the two sampling campaigns performed in winter 2009 and in winter 2010, respectively (triplicate water samples for each station and during 2 years, meaning n=6). These two consecutive years were similar in terms of discharge and concentrations along the river course and no outliers were present and discarded. Moreover, both years were

Tab. 1. The boundary conditions at the upstream and downstream for calibration data.

Parameter	Unit	Upstream boundary water quality	Downstream boundary water quality
Flow	m^3 s^{-1}	60.00	-
Temperature	°C	5.70	6.80
Conductivity	µS cm^{-1} 25°C	271.00	540.00
Inorganic Solids	mg D L^{-1}	0.90	24.45
Organic Nitrogen	µg N L^{-1}	11.47	335.17
NH_4-N	µg N L^{-1}	25.50	129.50
NO_3-N	µg N L^{-1}	851.50	5316.00
pH	-	8.20	8.13

characterized by dry winter and by deep groundwater level (no active springs along the investigated sector). We therefore considered such winter calibration as appropriate to characterize the system when no river-groundwater interactions occur.

An automatic calibration procedure was used for NO_3-N, NH_4-N, organic N, TN, EC and discharge. To minimize the error between simulation results and measured data, the 9 constants of inorganic suspended solid (ISS), organic N, NH_4-N and NO_3-N had to be adjusted (Tab. 2). The calculation time step was settled at 2.8 minutes to ensure that the model is steady-going. The integration solution was handled with Euler method (Chapra and Pelletier, 2003). The model was run until the system parameters were appropriately adjusted and a reasonable agreement was achieved between model results and field measurements. The model was run using a completely different data set for winter 2012 to test the ability of the calibrated model to predict water quality and quantity under various conditions (validation process). The calibration and validation accuracy was tested using statistics based on calculation of normalized objective function (NOF), Coefficient of Determination (R^2) and Nash-Sutcliffe model efficiency coefficient (E):

$$NOF = \frac{\sqrt{\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}}}{O_{mean}} \quad \text{(eq. 3)}$$

$$R^2 = \left(\frac{\sum_{i=1}^{n}(O_i - O_{mean})(P_i - P_{mean})}{\sqrt{\sum_{i=1}^{n}(O_i - O_{mean})^2}\sqrt{\sum_{i=1}^{n}(P_i - P_{mean})^2}}\right)^2 \quad \text{(eq. 4)}$$

$$E = 1 - \left(\frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(O_i - O_{mean})^2}\right) \quad \text{(eq. 5)}$$

Where P_i and O_i are the predicted and measured values, respectively; O_{mean} is the mean of measured values; and n is the number of measurements. Model predictions are acceptable for NOF values in the interval from 0.0 to 1.0 (Gikas, 2014). Nash-Sutcliffe efficiency can range from $-\infty$ to one. An efficiency of one (E=1) corresponds to a perfect match of modeled simulation to the observed data (Nash and Sutcliffe, 1970). The coefficient of determination ranges from 0 to 1 (Steel and Torrie, 1960).

The model was run with data of each summer of the three years from 2009 to 2011, using the calibrated constants reported in Tab. 2. A unique set of calibrated constants was used for the whole river, that has a considerable length (154 km). This is an approximation of the reality and represents a limit of the software used. However, the simulation of water chemistry by QUAL2Kw was satisfactory, in particular in the upstream sector of the Oglio River that is targeted by our study.

After running the model, contrarily to winter simulations, a gap was found between predicted and measured parameters (discharge, EC and NO_3-N). As all point pollution sources were monitored, we addressed such gap to river-groundwater interactions. Groundwater flow and groundwater attributes (NO_3-N and EC) were then compiled in the diffuse source reach of QUAL2Kw and the model was run again, until simulation approximately matched observations. In this iterative approach, groundwater input was chosen on the basis of the gap between measured and simulated river discharge while values of NO_3-N and EC were chosen on the basis of data from springs adjacent the river course (Laini *et al*., 2011). In particular, N-NO_3^- concentration ranged between 2 and 20 mg N-NO_3^- L^{-1} while EC ranged between 250 and 2000 $\mu S\ cm^{-1}$. We preferred to use springs chemistry and not wells chemistry because the surficial portion of underground water that feeds the springs adjacent the river is the same portion that interacts with the river water. We attributed the gap between modeled and experimental data to diffuse pollution, including river-groundwater interactions, as all point sources, including direct inputs from springs, were monitored.

Tab. 2. QUAL2Kw estimated constants and their minimum and maximum values for the Oglio river.

Parameter	Constant	Calibrated values	Min.	Max.
Inorganic suspended solids	ISS settling velocity (m d^{-1})	1.44	0	2
Organic N	Organic-N hydrolysis (d^{-1})	0.293	0.05	0.25
	Temp correction	1.00	1	1.07
	Organic-N settling velocity (m d^{-1})	1.69	0.05	2
NH_4-N	NH_4-N nitrification (d^{-1})	0.165	0.05	3
	NH_4-N Temp correction	1.01	1	1.07
NO_3-N	NO_3-N denitrification (d^{-1})	0.472	0	2
	NO_3-N Temp correction	1.04	1	1.07
	Sediment denitrification transfer coefficient (m d^{-1})	0.90	0	1

RESULTS

Winter and summer chemistry in the Oglio River water

The Oglio River discharge and chemistry were different in the winter and summer that are within the non-irrigation and irrigation periods, respectively. Previous studies in this basin suggest that differences in hydrology associated to water abstraction and irrigation are likely more important as drivers of river chemistry than differences in water temperature and in within river processes (Bartoli *et al.*, 2012; Sacchi *et al.*, 2013; Delconte *et al.*, 2014).

In both seasons, the target parameter of this study (NO_3-N, that constitutes most of the TN pool) exhibited an increase along the river course, that was steeper and larger in summer than in winter (Figs. 3, 4, 5 and 6). The same trend was evident for EC and for dissolved inorganic carbon (not shown here). Difference in discharge trends reflects river water use in summer with large abstraction in the upstream sector that results in a minimum river flow just after the last diversion and in a progressive discharge increase downstream it (km 35). During winter, on the contrary, discharge increases from upstream to downstream as diversions do not operate. In the summer, the Oglio River midstream chemistry (EC, NO_3-N, inorganic carbon measured downstream the last diversion infrastructure) resulted very similar to that of a number of springs located in the proximity of the river course (Laini *et al.*, 2011).

Model calibration and validation

The large available dataset allowed a precise calibration of the model (Fig. 3a). Results from the calibration and validation showed in general a good correspondence between calculated and experimental values for most of water quality variables and in particular for EC and the oxidized form of inorganic N. The final

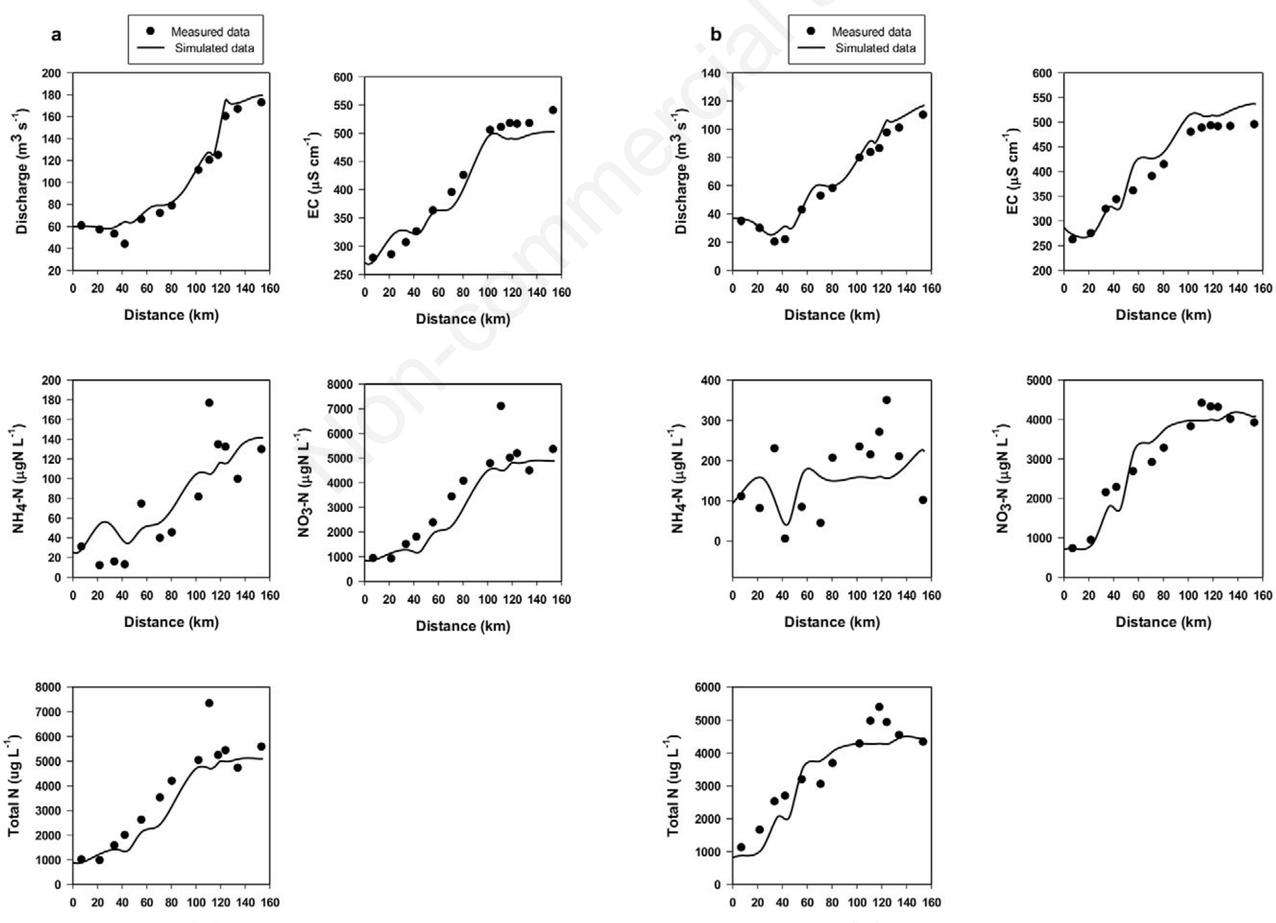

Fig. 3. The calibration (a) and validation (b) results of measured and simulated data with QUAL2Kw for the Oglio River. Calibration was performed with winter data from 2010 and 2011 (average data) while validation was performed on winter 2012 data.

estimated values for the QUAL2Kw parameters and their minimum and maximum ranges are shown in Tab. 2. QUAL2Kw calibration requires additional parameters (as for example stoichiometry of organic matter) that are not reported in Tab. 2 as they are default parameters of the model. During validation, discharge in the downstream portion of the Oglio River was slightly underestimated while NH_4-N, that represented a minor fraction of inorganic N (<10%), exhibited an erratic trend along the river course. The rather good calibration and validation of the model is supported by NOF, R^2 and E values for discharge, NO_3-N, NH_4-N and EC, reported in Tab. 3.

Simulation QUAL2Kw with summer data

After run the model with the summer data of 2009 to 2011, a big gap between the measured and simulation data was found for discharge, NO_3-N, EC and TN (Figs. 4a, 5a and 6a). In the summer, NH_4-N represented a minor fraction of total N in the Oglio river and the simulation of its

Tab. 3. NOF, R^2 and E values for calibration and validation of the model.

Parameter	Calibration			Validation		
	NOF	R^2	E	NOF	R^2	E
Discharge	0.28	0.9386	0.698	0.28	0.9359	0.600
EC	0.08	0.9732	0.876	0.05	0.9823	0.932
NH_4-N	0.39	0.8439	0.678	0.54	0.6623	0.535
NO_3-N	0.30	0.9072	0.655	0.13	0.9571	0.895
TN	0.29	0.9159	0.674	0.18	0.9312	0.747

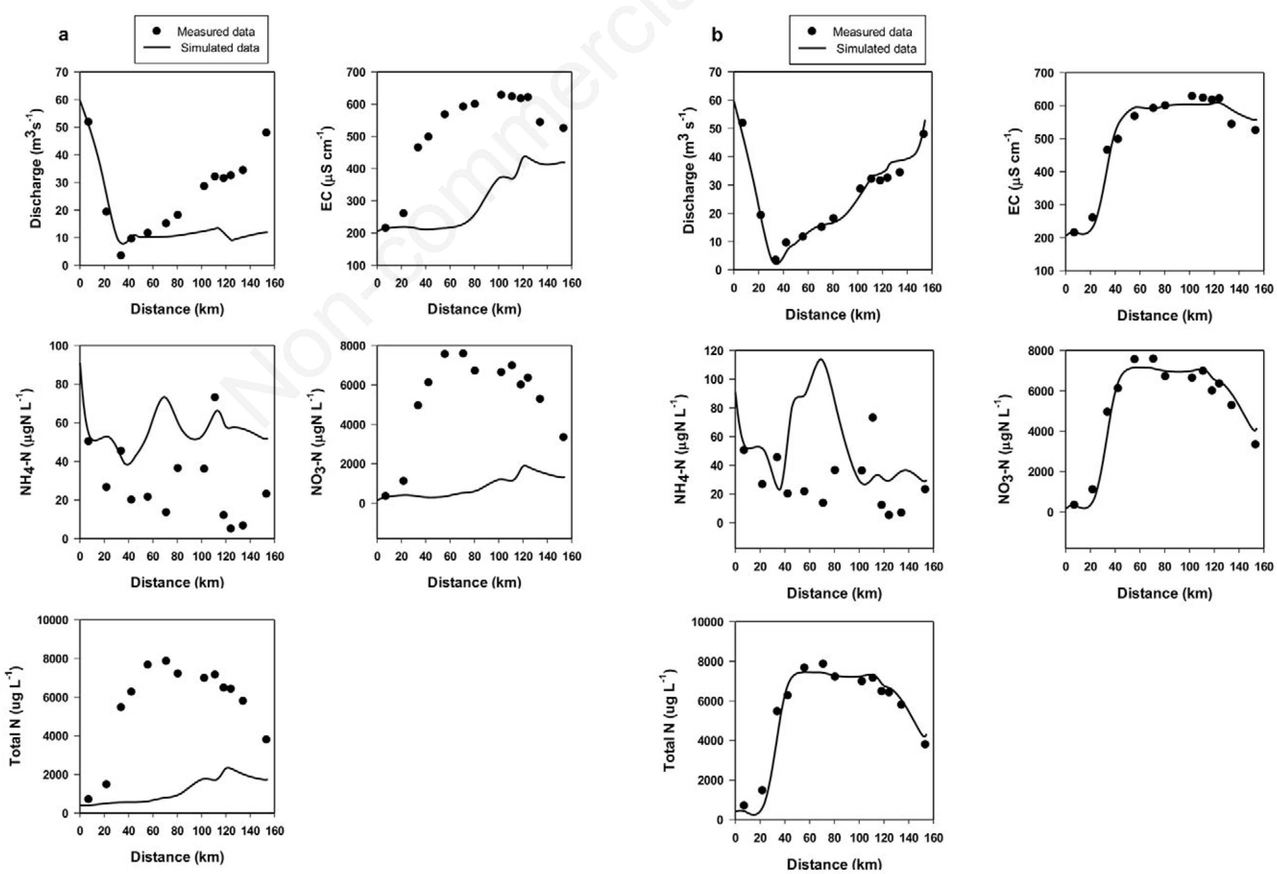

Fig. 4. Results of simulation of QUAL2Kw in summer 2009 without groundwater interaction (a) and with groundwater interaction data (b). Black dots represent measured data.

concentration was acceptable. The large data availability and detailed knowledge of this riverine system, of the whole set of water abstraction and point inputs allow to exclude unconsidered tributaries as responsible for the gaps between measured and modeled data. Moreover, the missing discharge has the order of magnitude of several m^3 s^{-1}, which is a large amount as compared to the errors associated to the relatively low summer discharge of the Oglio River, generally within 5% of measurements and thus of the order of hundreds liter per second.

As introduced earlier, our hypothesis for such gap is a large, diffuse input of nutrient-rich water from the groundwater along the river course, resulting in increase in discharge, EC, NO_3-N and TN concentrations. The groundwater contribution to the streamflow was calculated with mass balance and put as a diffuse source input parameter to QUAL2Kw, while the concentration of NO_3-N in groundwater were estimated from Laini *et al*. (2011), until simulation approximately matched observations. After setting these new inputs, the new run resulted in simulations much closer to experimental data (Figs. 4b, 5b and 6b). For summer 2009 the comparison between experimental and simulated data suggests that in the upstream portion of the river (km 0 to 20) there is a very limited water (and N) exchange between groundwater and the Oglio River. The results also revealed that the discharge of groundwater did not enrich the river with NO_3-N in the portion from Km 140 to 154 (Fig. 7). The same trend was observed in 2010 and 2011 (Figs. 5 and 6). This is in agreement with completely different soil in the upstream and downstream sectors of the river, resulting in NO_3-N rich water inputs (upstream, gravel soil where oxidative processes as nitrification dominates, as supported by low NH_4-N) and NO_3-N depleted water inputs (downstream, clay and silty soils, where denitrification likely dominates). The downstream input of NO_3-N depleted water would also explain the dilution of NO_3-N concentrations in the lower sectors of the river.

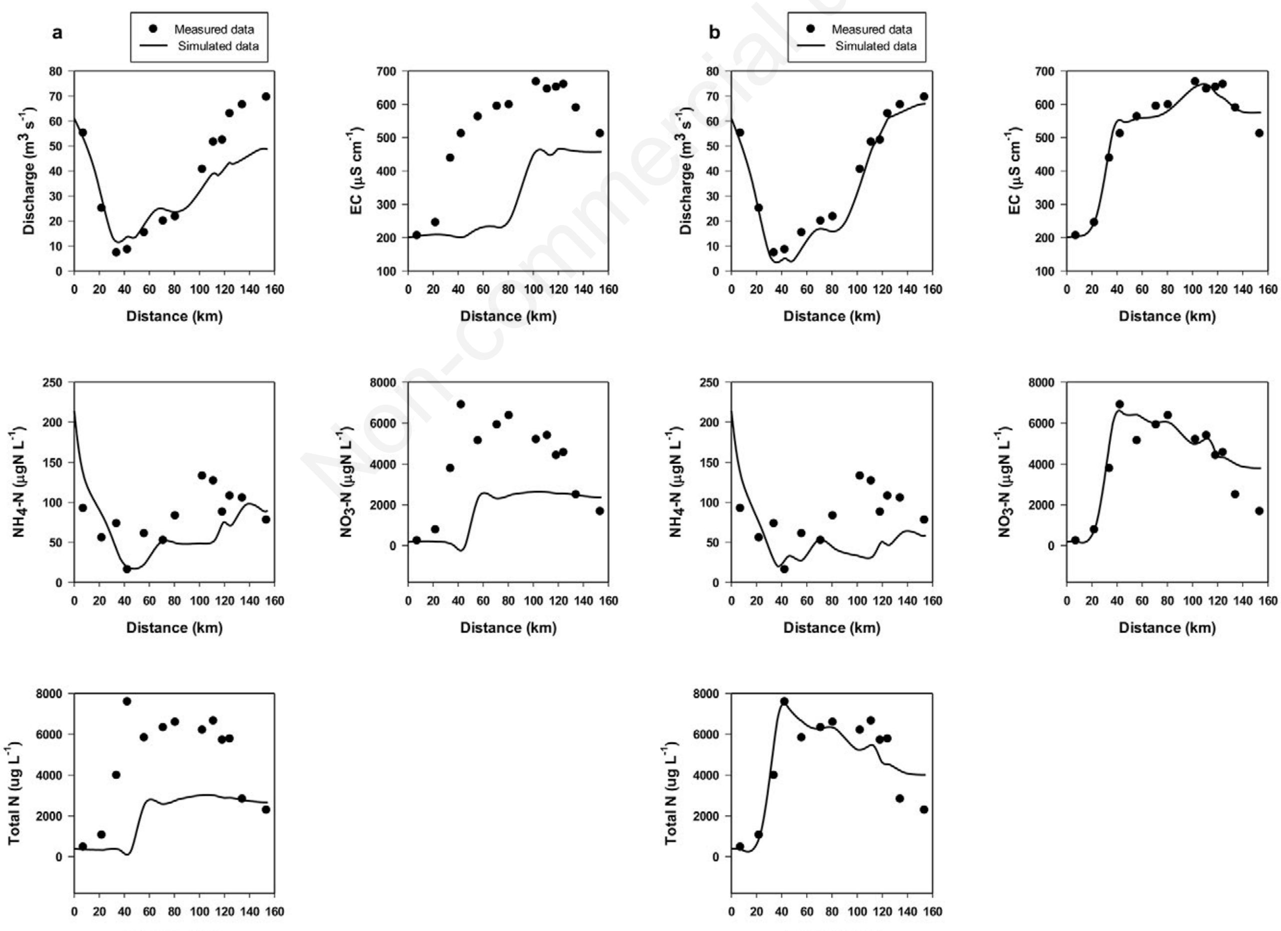

Fig. 5. Results of simulation of QUAL2Kw in summer 2010 without groundwater interaction (a) and with groundwater interaction data (b). Black dots represent measured data.

The highest input of NO_3-N along the Oglio River occurred consistently in the three years in the upstream reach, between Km 20 and Km 50, where the river crosses the higher permeability aquifer portion and the spring belt area (Fig. 1). This is reasonable as in this portion of the watershed, in particular in the summer and mostly due to flood irrigation, the groundwater table level is very close to the surface and higher than the river head. The result showed that the groundwater inputs to the river are not homogeneous along the segment and the most NO_3-N enters to the river, between km 20 and km 120. Taking into consideration the available information, the heterogeneous distribution of this input can be explained by (in agreement with the Darcy's Law) i) the heterogeneity within the finer-grained sediments, resulting in differences in terms of hydraulic conductivity of the medium along the river, and ii) the observed variations in terms of hydraulic gradients between river and groundwater. Filling the gap between measured and modeled data allowed to calculate, along the river course, the total amount of water and the load of NO_3-N entering into the river from groundwater. We estimated that some 25.17, 25.63 and 29.89 ton per day of NO_3-N were exchanged from the groundwater to the Oglio River during summer 2009, 2010 and 2011, respectively (Fig. 7). These values of NO_3-N loads to the river are considered high, as they are roughly equivalent to the daily amount of N produced by a population between ~200,000 and ~250,000 AE. A probable cause for this is the intense fertilization of the area which enriches the river with oxidized forms of inorganic N. Result of NH_4-N showed that agricultural activities did not enrich the river water in the three years studied and that there are no processes in the river and in the groundwater that results in the accumulation of NH_4-N.

DISCUSSION

The model we have used for our simulation proved to be reliable and to provide good fitting between

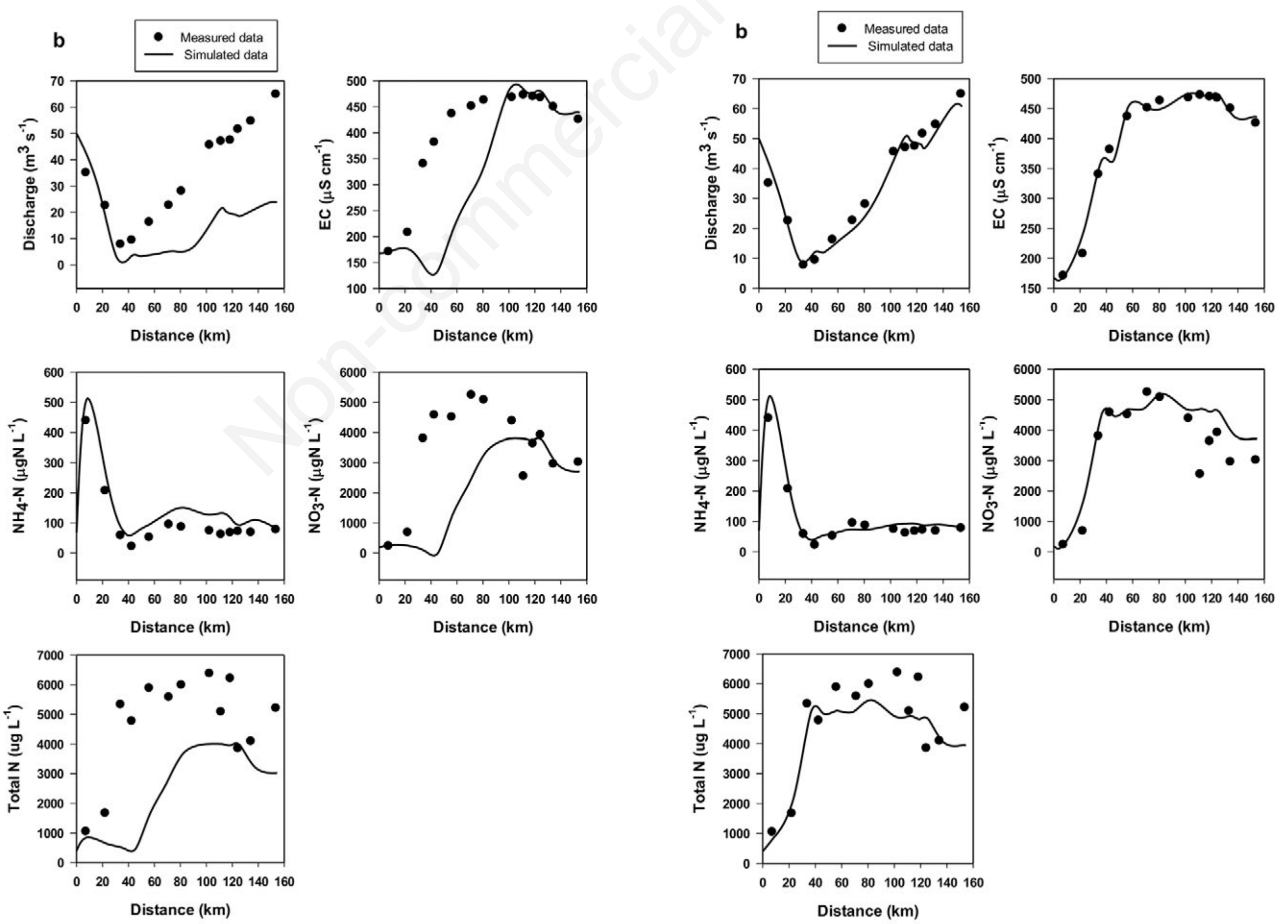

Fig. 6. Results of simulation of QUAL2Kw in summer 2011 without groundwater interaction (a) and with groundwater interaction data (b). Black dots represent measured data.

experimental and modeled data for winter. Our work suggests also that QUAL2Kw, at least when a robust dataset of discharge and water chemistry is available, can be used to estimate unknown values of parameters as the total input and the location of the river-groundwater interaction. This is supported by previous work carried out with different approaches but leading to similar estimates of NO_3-N groundwater-river exchange (Bartoli *et al.*, 2012).

In this application, the accuracy of QUAL2Kw relies on the large dataset available for the Oglio River, that was intensively studied in terms of water chemistry (Strategies for requalification of Oglio River project), multiple pressures at the watershed level (Lombardy Foundation for the Environment project targeting N genesis, fate and transport) and minimum vital flow (Oglio Consortium and Lombardy Region project) along 2007-2015. Similar results cannot be obtained in the absence of detailed information about river water chemistry and discharge and about the complete inventory of point sources in terms of discharge and chemistry. Moreover, we were able to fill the gap between measured and modeled data as we knew the chemistry of groundwater, leaving as unknown parameter only water input from the groundwater.

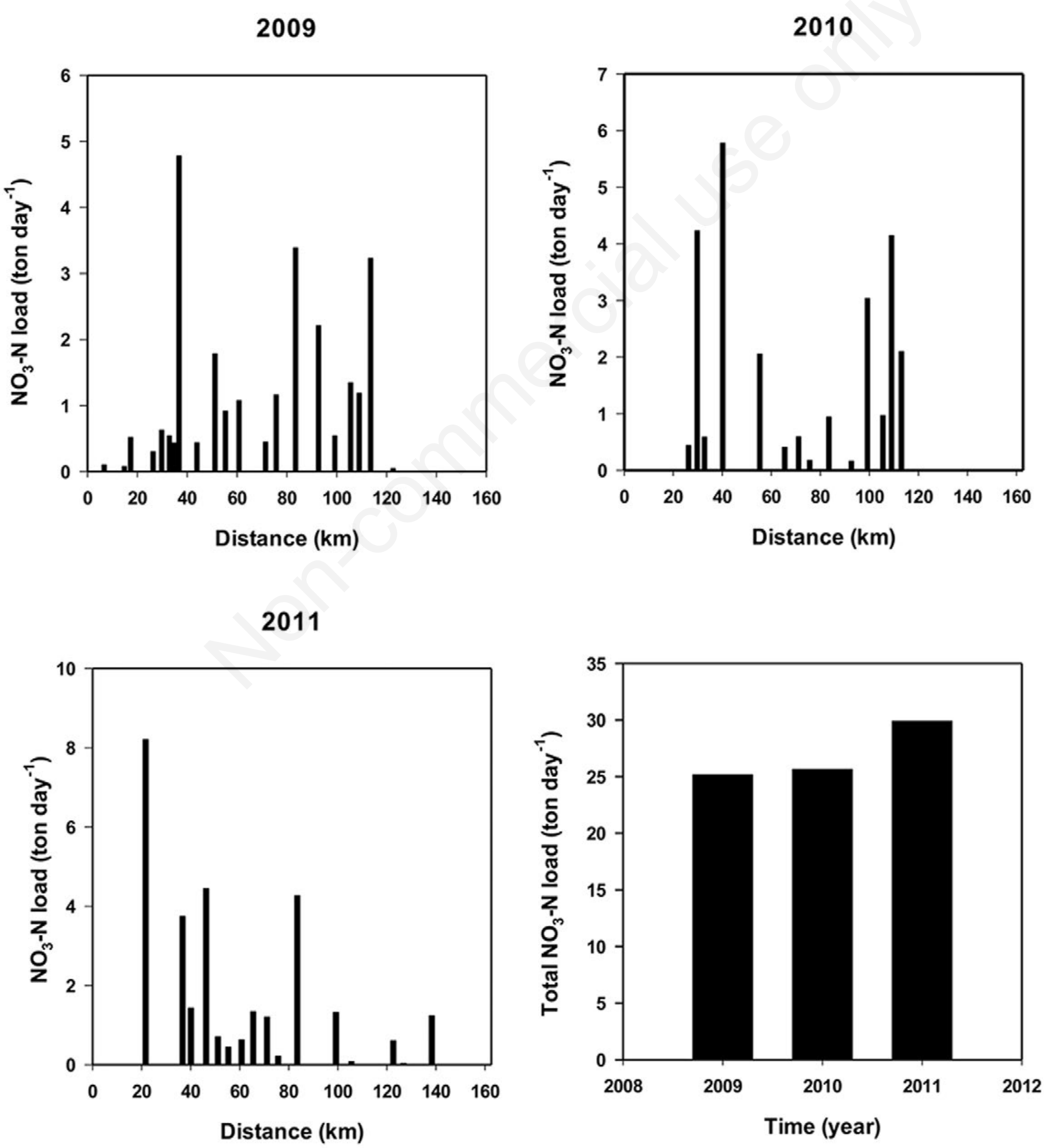

Fig. 7. Nitrate loads estimated for the Oglio River basin in the summer of 2009, 2010 and 2011.

In the study period, our results suggest a relatively small interannual variability of river-groundwater interaction and N exchange, that change in consecutive years by nearly 25%. Viaroli *et al.* (2018) report much larger interannual variations of N loads exported from the Po River, sometimes by 100%. Different levels of river-groundwater interactions may be expected in years with different precipitation patterns or with different timing of precipitation. Rain, together with irrigation water, may explain the vertical migration of the water table before or during the irrigation period but also the concentration of NO_3-N. Prolonged water saturation, even in gravel soil, may in fact promote high rates of NO_3-N removal via denitrification. This is something that was measured in the downstream sectors of the Oglio River, where our experimental and simulated data support diffuse inputs of groundwater but depleted in NO_3-N and therefore diluting river concentrations.

Until relatively few years ago, rivers and their functioning were not central in research and restoration ecology. Hydrology was the main research area dealing with lotic environments, due to practical and very relevant reasons, among which the control of flooding, the minimization of risk for population, the use of water for irrigation and for the production of electricity. The Alpine sector of the Po River plain hosts a series of large lakes feeding rivers among which the Oglio River, all regulated since the beginning of the last century. Regulation (www.laghi.net) starts at the very beginning of each river through a dam that simultaneously controls the level of water in lakes and releases a known discharge in each river. The regulation practice is optimized and adapted in almost real time to the local meteorology by varying the discharge as a function of water inputs to lakes. The optimization allows to accumulate water during winter within the lakes and release it during the irrigation period. The optimization therefore guarantees acceptable summer level in lakes for tourism and navigation purposes and large water availability for irrigation and electricity production.

A second discharge regulation level includes a number of water abstraction infrastructures, some of which were realized up to 500 years ago and distributing water capillary within the watershed. Such regulation and infrastructures have allowed this area to develop a solid economy based on agriculture, animal farming and industry.

Simultaneously, it has deeply changed the hydrology of a huge area: irrigation is in fact based on flooding over 66% of permeable soils in a period where precipitations are low while river discharge (and the recharge of the aquifer) is maintained at minimum during autumn, winter and spring. As a result, the groundwater undergoes pronounced seasonal vertical migrations that are mostly driven by irrigation and not by the natural water cycle. This is supported by discharge data of the numerous springs located in the spring belt area, that are null for most of the year with the irrigation period (June-September) as exception (De Luca *et al.,* 2014).

Water abstraction were (and still are) traditionally concentrated in the upstream sector of the rivers, very close to the lakes, likely due to the relatively higher height over the sea level and the possibility to distribute the water with artificial canals over longer distances. This was also due to the fact that in the past the springs were feeding the river with high quality water, replacing the water abstracted for irrigation. This is why in some situations (the Oglio River for example) it was allowed to divert 100% of the natural discharge with the abstraction infrastructures along the initial 29 Km, which is to say that the river was completely dry at Km 30 due to irrigation and that the downstream discharge was entirely guaranteed by river-groundwater interactions and by downstream point sources. Now the situation is slightly different due to a legislation that does not allow to dry rivers; on the contrary consortiums should always leave in the river at least the 10% of the natural discharge.

Such situation can be clearly seen by comparing experimental and simulated discharge data of the non-irrigation (winter) and irrigation (summer) periods. In the latter, discharge displays a sudden and dramatic drop due to a series of abstractions all located in the upstream sector (see the scheme of Fig. 2). Summer graphs also show that discharge, just after reaching a minimum, start to increase due to large inputs from the groundwater, reaching in some sectors exchange rates up to 2.11, 1.82 and 1.67 $m^3 s^{-1} km^{-1}$ for summer 2009, 2010 and 2011, respectively.

A major difference with the past is that the development of intensive agriculture and animal farming of the last decades has resulted simultaneously in a deep change of N cycling (Ascott *et al.,* 2017). Previous studies in this and other similar areas with large water availability have demonstrated a large N excess in agricultural soils, mostly due to excess manure, excess use of synthetic fertilizers and flooding irrigation (Bartoli *et al.,* 2012; Vassena *et al.,* 2012; Delconte *et al.,* 2014). They have also demonstrated a continuous and ongoing accumulation of reactive N in the groundwater, down to 200 m depth (Ascott *et al.,* 2017). The quality of groundwater in some areas of northern Italy is worse than that of the surface water and results in increasing costs for depuration and human use (Sacchi *et al*., 2013). As compared to the past, the groundwater that replaces the abstracted river water along its course is NO_3-N rich and it affects the chemical quality of the whole river, by largely increasing the NO_3-N concentration measured in the Iseo Lake.

Under these circumstances it is urgent to change the ongoing practices, including N-management in agricultural areas as well as water use. What is evident is that climate is rapidly changing also in these geographical areas, with much lower precipitation and an increasing number of consecutive days with high temperatures, as different models predict (Pasini *et al.,* 2012; Cifrodelli *et al.,* 2015; Pedro-Monzonís *et al.,* 2016).

A whole system designed and managed for large water availability (*i.e.* water demanding maize as dominant crop, flooding as main irrigation practice) seems extremely vulnerable to climate change and actions should be urgently discussed at the political level. It is difficult to predict the fate of excess N under scenarios of different water availability and use: it is likely that discharge will decrease and will not be replaced by groundwater due to its deep level. It is also likely that NO_3-N will accumulate and concentrate in the groundwater, with limited transfer to the surface water (Ascott *et al.,* 2017). QUAL2Kw could be a good tool to simulate discharge and chemistry under variable scenarios of water availability from lakes, basin, point and diffuse sources but it has a number of limitations. For example, calibrated constants were assumed to be the same along the whole Oglio river, which is probably not true (Potts, 2014). Moreover, QUAL2Kw cannot simulate branches of the river systems (Liangliang and Daoliang, 2015) and it cannot be applied under non-uniform mixing (2D or 3D)and unsteady flow, and to simulate watershed processes, and sediment adsorption/desorption.

CONCLUSIONS

We report an alternative application of QUAL2Kw targeting the indirect estimates of river-groundwater interaction in terms of exchanged water and NO_3-N. Results align with previous measurements and estimates, based on mass balance of conservative and non-conservative solutes. Results from this and previous works suggest a deep alteration of hydrology and nutrient (N in particular) cycling in agricultural, irrigated watersheds. They suggest that the groundwater recycles to surface water large amounts of reactive N and that the groundwater is a site of accumulation of NO_3-N that can promote long-term eutrophication of rivers and downstream aquatic environments. The slow turnover of groundwater and the limited knowledge of the effect of climate change in this geographical area are elements of concern. It is in fact difficult to predict the temporal lag between political actions targeting water and fertilizer use optimization and significant reduction of NO_3-N concentration in groundwater and river water.

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