DOI: 10.4408/IJEGE.2021-01.S-21

CAN'T TELL A BOOK BY ITS COVER: DISJOINTED GROUNDWATER CONTAMINATION AND LAND USE IN AN ALLUVIAL AQUIFER OF NORTHERN ITALY

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EXTENDED ABSTRACT

La Pianura padana è caratterizzata da un'intensa attività agricola e zootecnica che nel corso dei secoli ha profondamente alterato l'aspetto e il funzionamento degli ecosistemi originari. Nella zona settentrionale del bacino del fiume Po, in special modo in Lombardia, le pratiche agricole e zootecniche sono supportate da una grande disponibilità idrica. Dall'inizio del medioevo, un capillare sistema di canali ha permesso di derivare grandi quantità d'acqua dagli emissari dei laghi subalpini. Negli anni Cinquanta del ventesimo secolo gli enti regolatori hanno realizzato all'origine degli stessi emissari un complesso sistema di ponti-diga, che permette di modulare i rilasci in base alle necessità turistiche, idroelettriche e soprattutto irrigue, erogando volumi maggiori durante il periodo irriguo (aprile-settembre) e accumulando acqua nei laghi subalpini durante il periodo non irriguo.

Nell'area di studio, individuata lungo il corso del fiume Mincio, l'irrigazione a scorrimento permette la crescita di colture idricamente esigenti in suoli caratterizzati da elevata permeabilità. L'alta concentrazione di allevamenti (sia suini che bovini) comporta la produzione di grandi quantità di liquami, il cui spandimento avviene in suoli già identificati come zone vulnerabili ai nitrati (ZVN). La triplice interazione tra la permeabilità dei terreni agricoli, i grandi volumi irrigui e le fertilizzazioni rappresenta un grande rischio potenziale per la qualità della risorsa idrica, sia superficiale che sotterranea. Altri autori hanno infatti evidenziato in quest'area geografica problematiche relative alle concentrazioni elevate di nitrati, sia in falda che lungo il corso del Fiume Mincio.

In questo studio, che si inquadra in un più ampio progetto di caratterizzazione idrogeologica dell'area, viene caratterizzata la contaminazione da nitrati nella falda freatica in relazione ai diversi utilizzi del suolo in sinistra e destra idrografica. Le due aree nelle rispettive sponde, seppur con categorie simili, sono caratterizzate da percentuali diverse d'uso del suolo (e.g. i seminativi corrispondono al 92.15% dell'area in destra idrografica e al 41.34% in sinistra idrografica), che comportano anche pressioni differenti verso l'idrosfera.

Nell'ottica di confrontare come il diverso uso del suolo influenzi i parametri qualitativi e quantitativi della falda, è stato eseguito un monitoraggio dei livelli piezometrici con cadenza mensile in diciassette pozzi, attestati nel locale acquifero non confinato, per valutare gli effetti della ricarica data da precipitazioni ed irrigazione. Contestualmente, sono stati prelevati campioni di falda per la misura di parametri chimico-fisici sul campo e l'analisi in laboratorio della silice reattiva disciolta (SiO_2) e dei principali anioni e cationi.

Dai risultati emerge come, in entrambe le sponde del Mincio, la falda fluisca verso il fiume, che svolge quindi un ruolo drenante. Durante l'autunno, la concomitanza dello spandimento dei liquami e delle abbondanti precipitazioni fa sì che la falda sia caratterizzata da alte concentrazioni di nitrato (NO_3^-) e SiO_2, riconducibili all'esteso uso di fertilizzanti di origine zootecnica. Le differenze nell'uso del suolo (e nelle conseguenti modalità di fertilizzazione ed irrigazione) tra la sponda sinistra e destra del Mincio non sembrano ripercuotersi nei parametri idrochimici e idrodinamici della falda. Se infatti le attività agricole (e non) in sinistra idrografica possono comportare un minore utilizzo di fertilizzanti rispetto alla destra, le concentrazioni rilevate di NO_3^- e SiO_2 sono comunque maggiori.

Questi risultati suggeriscono come la contaminazione da NO_3^- non dipenda solamente da un eccesso di fertilizzazione organica o di sintesi, ma sia anche localmente modulata da caratteristiche intrinseche dell'acquifero e della falda, quali ad esempio la dispersione idrodinamica e la capacità denitrificante. Vista l'azione drenante del fiume Mincio in questo settore del bacino, l'aumento della concentrazione di NO_3^- nelle acque del corso d'acqua dipende anche dagli apporti di acque di falda fortemente contaminate da questo ione.

Queste considerazioni risultano utili alla comprensione delle dinamiche idrochimiche ed idrodinamiche della falda a livello locale in aree classificate come ZVN e potrebbero essere integrate nei processi decisionali nella regolamentazione delle attività di spandimento dei liquami, in ottica di salvaguardia ambientale sensu Direttiva Quadro sulle Acque (2000/60/EC) e Direttiva Nitrati (91/676/EEC).

ABSTRACT

In the Po plain, intensive agriculture is supported by large irrigation volumes and use of fertilizers. We analysed the effects of different land uses in a sector of the Mincio River on groundwater hydrochemical characteristics and hypothesized local regulation of NO_3^- contamination. In the unconfined coarse-grained alluvial aquifer, hydraulic heads were measured monthly in 17 wells from May 2019 to December 2019, to trace how the aquifer recharge and manure spreading influence groundwater physico-chemical parameters and quantity. The experimental site was divided into two different zones on the left and right bank characterized by different land use. Although these dissimilarities concern different irrigation and fertilization practices, we measured in both areas nitrate (NO_3^-) contamination in groundwater, with concentrations exceeding legislative limits by a factor of 2. Our results suggest that NO_3^- contamination in this area is not only driven by specific land use and related agricultural practice; rather, other local factors intrinsic to the local aquifer and groundwater characteristics play an important role. Presented results on groundwater quality and quantity provide useful information to increase knowledge on local N dynamics and to the administrations regulating fertilizer use in this area, already reported as Nitrate Vulnerable Zones (NVZ).

Keywords: *land use, nitrate pollution, Mincio River*

INTRODUCTION

The combination of intensive agriculture and livestock production represents a stressor for the hydrological and nutrient cycles in lowland ecosystems. Some of these anthropogenic pressures determine the variation of nitrogen (N), phosphorous (P) and silica (Si) biogeochemical cycles, leading to eutrophication and the degradation of the chemical and biological quality of the water bodies (Bernot & Dodds, 2005; Han & Allan, 2012; Mulholland *et alii*, 2008; Paerl, 2009). The European Union, to protect both surface- and groundwater from contaminants, enacted two directives (Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources, 1991; Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, 2000). However, there are still significant pressures from agricultural pollution affecting 38% of European water bodies (UNITED NATIONS WORLD WATER ASSESSMENT PROGRAMME, 2015).

In the Italian agricultural sector, the Lombardy Region (northern Italy), is one of the principal producers, with 41,120 farms and a utilised agricultural area (UAA) of 9583.78 km^2. At the same time, livestock production accounts for 1.44×10^6 cattle and buffaloes and 4.39×10^6 swine. The regional landscape and hydrosphere were deeply shaped to support these activities since Middle ages (Fantoni, 2008). The wide utilization of manure as fertilizer in these agricultural areas led the European Union to grant derogations on the Nitrate Directive to Lombardy Region and other areas of the Po Plain (Commission Implementing Decision of 3 November 2011 on granting a derogation requested by Italy with regard to the Regions of Emilia Romagna, Lombardia, Piemonte and Veneto pursuant to Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources, 2011), which were extended till 2019 (Commission Implementing Decision (EU) 2016/1040 of 24 June 2016 on granting a derogation requested by Italian Republic with regard to the Regions of Lombardia and Piemonte pursuant to Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources, 2016). As a result of these concessions on manure utilization as fertilizer, several authors reported in this area a large and widespread nutrient surplus using soil system budgets (Soana *et alii*, 2011; Viaroli *et alii*, 2018) and NO_3^- concentrations anomalies in the Mincio River (Pinardi *et alii*, 2018). In this area, a previous work (Severini *et alii*, 2020) reported the groundwater contamination by NO_3^- due to intense fertilization. The aim of this work is to merge the findings of these articles and investigate how differences in land use at local scale can affect groundwater physico-chemical parameters in a phreatic aquifer of northern Italy. To achieve this aim, a detailed hydrogeological characterization was carried out in two areas on the banks of the Mincio River with different land uses.

STUDY AREA

The study area (Fig. 1) is located along the Mincio River, between the municipalities of Volta Mantovana, Marmirolo and Valeggio sul Mincio (Mantua Province, Lombardy Region).

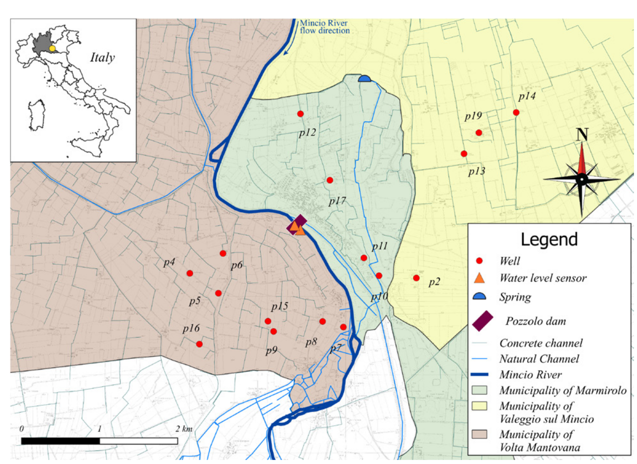

Fig. 1 - Location of the study area

Here, the right bank area of the Mincio River was previously investigated from the hydrogeological point of view (SEVERINI *et alii*, 2020)

On a regional scale, the experimental site belongs to the multilayer aquifer of the Po alluvial plain (Fig. 2), constituted by middle-upper Quaternary succession sediments (AMOROSI *et alii*, 2008). As reported in AMOROSI *et alii* (2008), the aquifer is characterized by a cyclic architecture of fluvial-channel facies (gravel and sand) and overbank facies (silts and clays).

The Mincio River, originating from the Garda Lake, flows for 75 km in the Po plain till the homonym river. From a geomorphological perspective, the Mincio dissects the Po plain's main level (GUZZETTI *et alii*, 1997) creating four orders of fluvial terraces (CHELLI *et alii*, 2018) and flows nowadays in Holocene deposits (MARCHETTI, 2002).

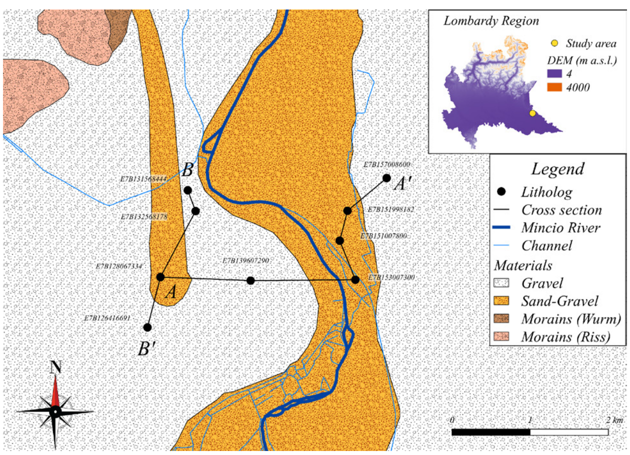

Fig. 2 - Geological map with digital terrain model of the Lombardy Region. AA' and BB' indicate the cross-sections reported in Fig. 3

Several dams control the hydrological regime of the Mincio River, adapting the river flow to the irrigation needs of the surrounding agricultural area. As a result, during the irrigation period (April-September), the river is characterized by a higher discharge (PINARDI *et alii*, 2018). The dams, together with several weirs, provide water for the capillary network of irrigation channels, both naturalized (i.e., with vegetated banks and bottom sediments) and completely artificial ones (i.e., made of concrete).

Land use

In the Mincio River basin, intensive agriculture holds a central role in economic activities. The UAA covers ~70% of the watershed (850 km^2), where the main cultivated crops are maize (30%), feed crops (27%), wheat (11%) and permanent grassland (9%) (ITALIAN NATIONAL INSTITUTE OF STATISTICS, 2011). At the same time, livestock farming is capillary performed in this area, accounting for 136×10^3 cattle and 483×10^3 swine, whose manure is used in the Mincio River basin to improve crop production (PINARDI *et alii*, 2018). In the arable land of the Mantua area, manure is usually applied in spring and autumn, in accordance with the preparation of the sowing season (PROVOLO & RIVA, 2003) and concurrently with the reaching of the volumetric capacity of the slurry tanks, forcing farmers to spread it (PEREGO *et alii*, 2012). The study area is located among three municipalities, namely Volta Mantovana, Marmirolo and Valeggio sul Mincio. Although agriculture is a pivotal activity in these areas, land use shows slightly differences among them. For example, the main land use category is arable crop in all the municipalities, with percentages of 68.74%, 58.5% and 66.62%, respectively. Similarly, the second most ample share in land use is meadow in Volta Mantovana and Marmirolo (17.72% and 28.56%, respectively) while in Valeggio sul Mincio it is permanent crop (18.09%). In general, land use categories are similar among these municipalities, but their different distribution could result in significant local changes.

Climate

According to the Köppen classification (KÖPPEN, 1936), the climate of the study area is humid and subtropical (Cfa) (PEEL *et alii*, 2007). Climatic data from the Goito meteorological station of the Regional Environmental Protection Agency of Lombardy (https://www.arpalombardia.it/Pages/Meteorologia/Richiesta-dati-misurati.aspx) show that the mean annual temperature is 14.2 °C, while the mean annual precipitation is 765.2 mm $year^{-1}$. The precipitation is higher in spring (197.6 mm) and autumn (248 mm) than in summer (157.1 mm) and winter (162.5 mm), according to data from the period 2005-2020.

MATERIALS AND METHODS

Hydrogeological Characterization

To reconstruct the geological architecture of the shallow unconfined aquifer, several lithological logs of boreholes were downloaded from the Lombardy region dataset (Banca Dati Geologica Sottosuolo della Regione Lombardia, 2020). In the wells screened within the study area, a monthly measuring time was adopted to reconstruct the variations in the hydraulic heads from June to December 2019 in 17 wells. Wells altitude (m a.s.l.) was calculated comparing the Regional Technical Map (CTR; 1:10,000 scale), the regional Digital Terrain Model (DTM, 5x5 m grid, https://www.geoportale.regione.lombardia.it/metadati?p_p_id=detailSheetMetadata_WAR_gptmetadataportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view&_detailSheetMetadata_WAR_gptmetadataportlet_uuid=%7BFC06681A-2403-481F-B6FE-5F952DD48BAF%7D, accessed on 4 January 2021) and, when available, the national Lidar dataset (±15 cm altimetric accuracy and ±30 cm planimetric accuracy). Data from two water level sensors (upstream and downstream the Pozzolo dam, Fig. 1) were downloaded from the

Interregional Agency for the Po River (Monitoraggio idrografico AIPo, 2021) and were used to include the Mincio river stages in the phreatic map reconstruction.

Precipitation data measured at the Goito meteorological station were obtained from the Agency for Prevention, Environment and Energy of Lombardy Region (ARPA Lombardia, https://www.arpalombardia.it/Pages/ARPA_Home_Page.aspx, accessed on 4 January 2021).

Sampling and physico-chemical analyses

Starting from July 2019, a bailer sampler was used to collect groundwater samples in the wells. The collected water was stored in 1 L polyethylene bottles and simultaneously electrical conductivity (EC), pH and temperature were measured using a multi-parameter probe (HI9829 HANNA Instruments, Woonsocket, RI, USA).

Successively, samples were filtered with a 0.7 µm pore size glass microfiber filters and stored according to the required analyses. For the dissolved reactive silica (SiO_2) analysis, samples were stored in 50 mL polyethylene bottles without ulterior filtering. Prior laboratory tests suggested no release of silica from the used filters (Grade GF/F, Whatman). For the ions analyses, samples were stored in 20 mL plastic vials after a sequential filtration with 0.2 µm pore size nylon filters. Additionally, samples for cations were acidified with 2M HNO_3 to avoid metal precipitation (Jenkins *et alii*, 1981). All the samples were stored in a refrigerated box until analyses, carried out within 24 h from collection.

In the laboratory, SiO_2 was analysed by spectrophotometry (Novaspec II Pharmacia) according to Golterman *et alii* (1978), while cations and anions were analysed by ion chromatography (883 Basic IC plus Metrohm, Herisau, Switzerland). Each chemical analysis was performed by the same operator on the same instrument using the same standards.

Land use

Land cover data for the study area were downloaded from the corresponding regional websites, namely Geoportale della Lombardia (http://www.geoportale.regione.lombardia.it/;jsessionid=38E4ADC6B7068023D8D3D0F1A8712DE6, accessed on 06 January 2021) and Portale Metadati Regione Veneto (https://idt2.regione.veneto.it/, accessed on 06 January 2021). Both datasets have a 1:10,000 scale and are updated to the latest version (2018). Spatial analyses on land cover data were performed within a GIS (QGIS version 3.10.12).

RESULTS

Geological and Hydrogeological reconstruction

Stratigraphic data granted the reconstruction of a reliable geological model of the experimental site, represented by two geological cross-sections (Fig. 3). It was possible to reconstruct the first meters of the cyclic architecture of fluvial-channel facies previously described (Amorosi *et alii*, 2008). Beneath the surface, the unconfined aquifer is characterized by gravel and subordinated sand. Its thickness varies between 30 m and 5 m moving from the external fluvial terraces toward the Mincio River. Under this permeable layer, a continuous bed of fine grain-sized deposits (namely silt and clay) has been observed, with a thickness always larger than 2 m.

As reported in Fig. 4, the irrigation recharge deeply influences the phreatic surface during the irrigation period, making the rainfall recharge negligible during these months, also due to the low amount of rain and the relatively high evapotranspiration. In July, groundwater head reaches the peak. Hydraulic heads are sensibly higher in the wells more distant from the Mincio River, like the well p4 where the hydraulic head is ~ 3.7 m higher than in December. From late August-

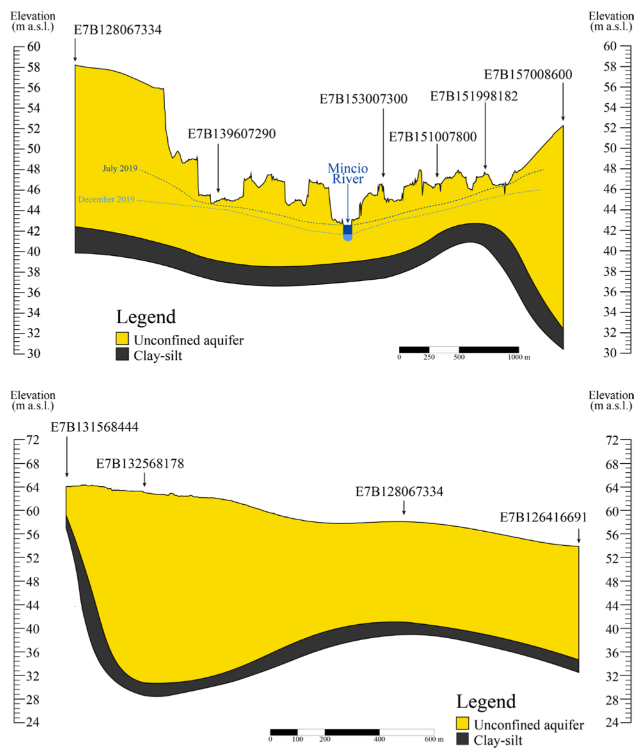

Fig. 3 - top) Geological cross-section AA' with hydraulic head surfaces of July and December 2019; bottom) Geological cross-section BB'. Arrows show lithological boreholes locations and the elevation profiles were calculated from the 5x5 m regional DTM. The location of both sections is shown in Fig. 2

mid September the irrigation is no longer performed and the phreatic surface begins to lower, till the minimum levels of the investigated time in December. During this period, the abundant precipitation registered by the meteorological station

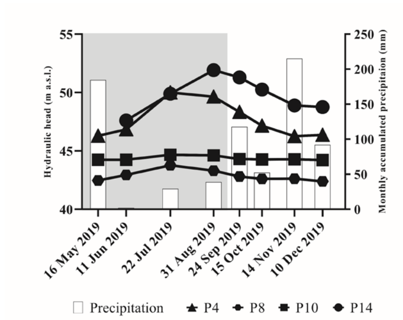

Fig. 4 - Groundwater level fluctuations in wells p4, p8, p10 and p14 (markers with straight lines) and monthly precipitation (bars). The grey area sets the irrigation period

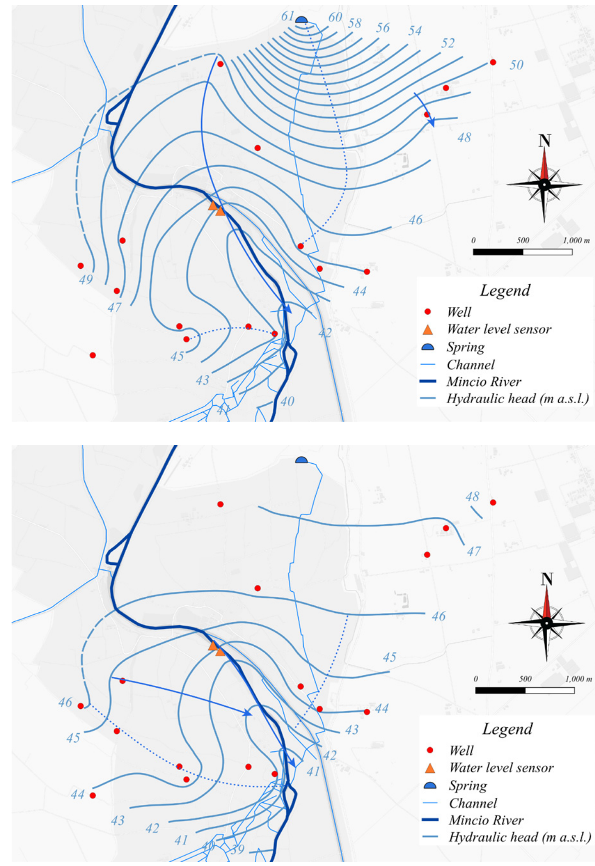

Fig. 5 - top) Net groundwater flow in July 2019, during the irrigation period; bottom) Net groundwater flow in December 2019. The dotted blue lines represent groundwater divides and the blue arrows drainage axes

in Goito partially compensates the lowering of the groundwater surface, like in November. Moreover, the quick response of the phreatic surface agrees with the high permeability of the aquifer and the low thickness of the unsaturated zone. The shallow groundwater flows toward the Mincio River, south-eastwards on the right bank of the river and south-westwards on the left bank (Fig. 5). Despite the seasonal fluctuation of groundwater heads, the groundwater flow showed only small variations during the investigated time. Overall, a main drainage axis is always observed among the Mincio River, which acts as gaining river downstream the Pozzolo dam. Moreover, a groundwater divide is always detected in the right bank, oriented NO-SE, but with slight changes during the investigated period. Another groundwater divide was described in the left bank, oriented N-S and with a different temporal extent. Temporary features of the potentiometric map include another drainage axis in the right bank during the non-irrigation period, while in the other bank an ulterior drainage axis of small entity is recognized during the irrigation period, oriented NO-SE. During the non-irrigation period, the hydraulic gradient has a mean value of 0.002 both in right and left bank areas. The higher values were measured near the Mincio River on the right bank (0.013). During the irrigation period, the higher hydraulic heads combined with the nearly constant (fixed and regulated) hydraulic head in the Mincio River result in an overall higher hydraulic gradient. On the right bank, the hydraulic gradient averages 0.004. In the left bank it has a mean value of 0.003, varying between 0.002 downgradient the well p12 and 0.016 downgradient the seasonal spring located in the northern part of the experimental site.

Hydrochemical characterization

Among all the measured parameters, only a few showed differences along the investigated period (Fig. 6), while the others remained nearly constant, or they were detected only sporadically (e.g. Na^+, K^+, F^-, NH_4^+ and NO_2^-).

Starting from the EC, all the groundwater samples showed an increase in October, when the EC peaked with 798 µS/cm. After that, EC remained generally constant in the left bank, whereas on the right bank it underwent some oscillations. Among cations, Calcium (Ca^{2+}) is the only one showing variations during the investigated period. No significant differences were observed between the two sides of the study area, although its values are slightly higher on the left bank of the experimental site. Both showed lower summer values, rising till the maximum concentrations measured in November and December. Also sulfate (SO_4^{2-}) exhibited higher concentrations in the eastern part of the study area. Nevertheless, sulfate dynamics showed similar trends on both sides, with higher concentrations in October and November and lower at the beginning and at the end of the sampling period.

SiO_2 values varied sensibly, with higher concentrations in November and December, measured in the eastern part of the study area. NO_3^- concentrations were higher in autumn and lower at the beginning and at the end of the sampling period. Some wells showed concentrations higher than the limit of 50 mg/L set by the national legislation for drinking water (Attuazione della direttiva

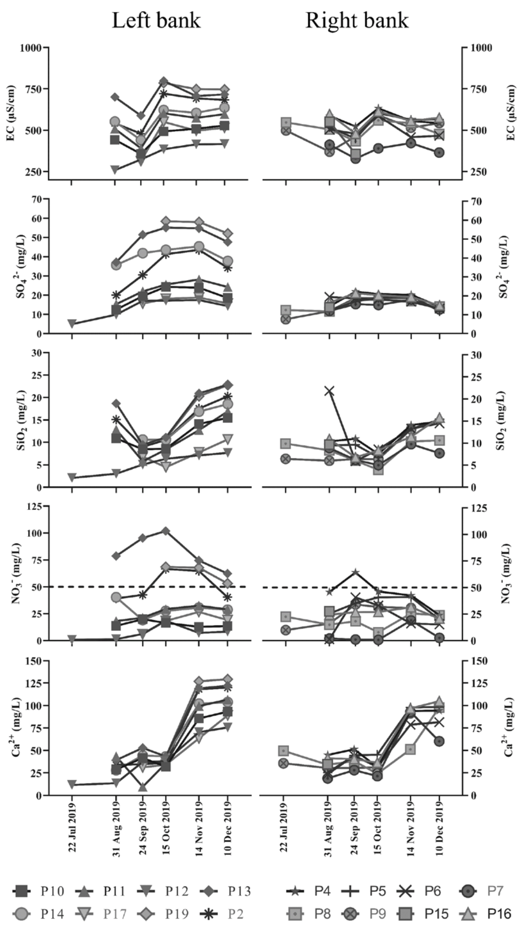

Fig. 6 - Main physico-chemical parameters of groundwater in the study area

98/83/CE relativa alla qualita' delle acque destinate al consumo umano, 2001) and the European Nitrates Directive (Directive 91/676/EEC of 12 December 1991 concerning the protection

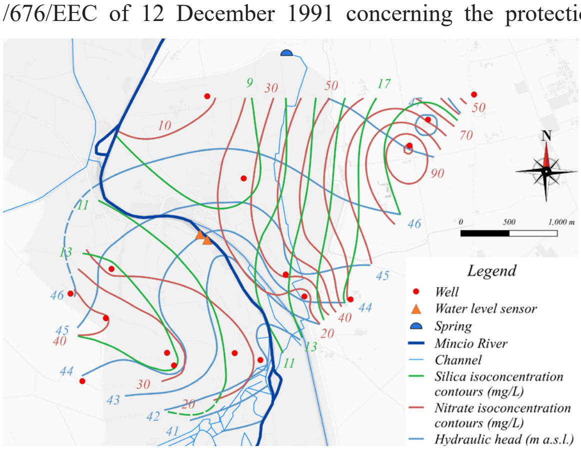

Fig. 7 - Distribution of NO_3^- and SiO_2 isoconcentration contours in the study area (November 2019)

of waters against pollution caused by nitrates from agricultural sources, 1991). The SiO_2 and NO_3^- isoconcentration contours overlap in the study area, showing also different behaviours in the left and right bank of the study area (Fig. 7).

Differences in land use

Land use was investigated in a 14 km² area around the wells (Fig. 8), of which 8.42 km² are on the left bank of the Mincio River and 5.58 km² are on the right bank. The western area is almost entirely used for arable crop (92.15% of total area) and meadow (5.73%), while permanent crops (mainly orchards) accounts for a low share (0.48%). The remaining categories account only for negligible fractions. The eastern zone shows the same principal land uses, but with different percentages (41.34%, 19.34% and 12.59%, respectively). Moreover, other categories hold a significant share, such as quarries (14.0%) and urban areas (4.58%). Differences in land use are reflected also in the extension of irrigation channels (Fig. 1). In fact, the lower surface of arable lands needing irrigation in the eastern area results in a shorter network of irrigation channels if compared to the other side. The density of irrigation canals in the two banks approaches 3.55 km and 4.73 km per soil square kilometre, respectively.

DISCUSSION

Land use in the investigated area

In the study area, land use data show significant differences between the eastern and the western zones. On the right bank of the Mincio River (western zone), the principal land use (arable crops) consists of maize cultivation and is irrigated via flooding

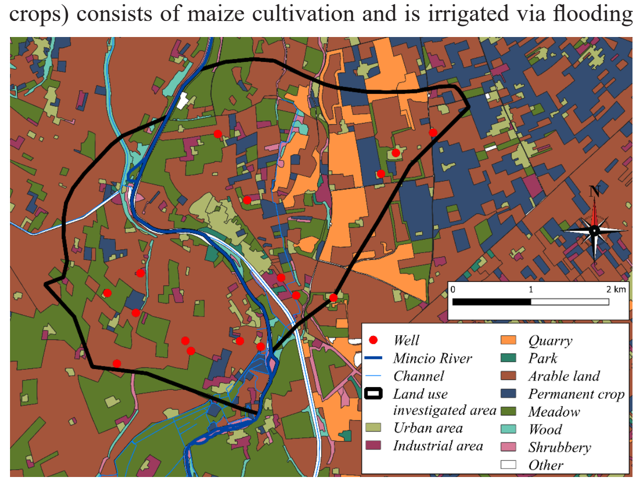

Fig. 8 - Land use in the two areas of the experimental site

(SEVERINI *et alii*, 2020). The second most common land use category is meadows (5.73%), used for fodder production. As reported by local farmers, these fields are usually fertilized in autumn and spring.

In the left bank of the Mincio River (eastern zone), land use is more heterogeneous. Arable crops remain the principal category, but sensibly less extended, as for meadows. Here, arable crops are committed not only to maize cultivation but also to horticulture, which involves different irrigation and fertilization practices (e.g. before transplanting and at the beginning of product development, as reported in PERSIANI *et alii* (2019) in other areas). Interviews with local farmers suggest that fertilization may occur every crop change, therefore multiple times per year. Unfortunately, land use data do not cover this level of detail, making it impossible to quantify the horticulture extension, which was only visually identified in the area. Another relevant category of land use in the left bank is the presence of quarries, which are not present in the right bank. As a matter of fact, there are several quarries in this area for the extraction of gravel, providing another evidence of the unconfined aquifer composition. Permanent crops cover a significant surface in the eastern zone. Their agricultural practices are different from arable land, with similar fertilization timing but likely with much smaller amounts. For example, in a nearby area of the Po Plain, TAGLIAVINI & MARANGONI (2002) suggested mineral N fertilization in orchards in spring, through the growing season and in September, with recommendations of 60 kg ha^{-1} of N for pome fruit and 100 kg ha^{-1} of N for peach.

In general, all the study area is characterized by an intensive agricultural activity, with different practices on the left and right banks of the Mincio River. Considering the high permeability of the soil and the aquifer, these activities can deeply affect the groundwater physico-chemical properties. Indeed, the study site is part of the NVZ, instituted by the Lombardy Region and Veneto Region after the assimilation of the Nitrate Directive. The effects of different agricultural practices on groundwater are usually investigated at regional scales and no data on the effects at local scales were reported for this area. This correlation will be discussed below.

Groundwater quantity and quality

The cyclic architecture proposed by AMOROSI *et alii* (2008) is confirmed at local scale. In the present experimental site, the aquifer is unconfined, superimposed to a continuous and thick bed of fine sediments. The hydraulic properties of the investigated aquifer have not been investigated yet, but other studies evaluated near the study area a transmissivity of 1.0×10^{-2} m^2s^{-1} and a storativity of 1.49×10^{-2} calculated through pumping tests (CHELLI *et alii*, 2018). In the investigated aquifer, during the irrigation period, the main recharge source is the irrigation water of the Mincio River, which largely exceeds the natural recharge given by precipitation. As a result, hydraulic heads in investigated wells can rise up to ~ 4.3 m. After the irrigation period, the aquifer recharge given by precipitation is considerable only during the rainier months, e.g. November 2019. During the non-irrigation period the phreatic surface is sensibly lower, with some shallow wells remaining dry (e.g., p15).

This behaviour of the phreatic surface is consistent with the right bank of the Mincio River, where arable land accounts for 92.15% of the total area and it is entirely devoted to maize cultivation. As a matter of fact, from late August to the end of September maize is harvested and irrigation is not performed anymore (PEREGO *et alii*, 2014), resulting in the lowering of hydraulic heads in the right bank area. The same seasonal pattern of groundwater heads was registered also in the left bank of the Mincio River. This is an unexpected result, as the different land use and agricultural practices should result in a smaller amount of irrigation water and in a consequently smaller aquifer recharge. Conversely, when irrigation is performed in the arable land of the left bank, it evidently provides a recharge volume comparable to the right bank, despite the lower flooding irrigated surface (41.34%). The influence of recharge from upstream the investigated area cannot be excluded, although arable crops (and consequently flooding irrigation practices) are less abundant upstream the study area.

Concerning the hydrochemical results showed in Fig. 6, in the study area NO_3^- shows higher concentrations during autumn, not simultaneously between the investigated wells. This is likely due to spatial nonsynchronous manure spreading and abundant precipitation in the study area, as happened from September to November 2019. The process regulating the spatial and temporal trend of NO_3^- concentrations in groundwater has been reported in SEVERINI *et alii* (2020). In this article it was postulated how the aquifer recharge with N-rich water can lead to the formation of a temporary layer with oxic conditions in groundwater, resulting in high NO_3^- values. On the contrary, when there is no more recharge given by irrigation or precipitation, this layer is no more present and the lower oxic conditions of groundwater promote denitrification, reducing NO_3^- concentrations. Although this process was demonstrated only in the right bank of the Mincio River, it can be reasonably extended to the left bank, as part of the same aquifer with similar agricultural practices. In the right bank of the study area, dissolved NO_3^- contours agree with groundwater path, decreasing along the hydraulic gradient due to hydrodynamic dispersion and denitrification, with major nitrogen sources located upstream and not above the study area (Fig. 7), as reported in SEVERINI *et alii* (2020). In general, NO_3^- isoconcentration contours in the left bank display a reasonable agreement with groundwater flow path. The decrease of NO_3^-concentrations along the hydraulic gradient is more emphasised than in the right bank, underlying a stronger effect of denitrification. Moreover, in addition to the concentrations coming upstream the study area, nearby the well p13 a contamination source was identified, where the maximum NO_3^- concentrations of all the study area were measured (101.97

mg/L, October 2019). This can be related to the arable land upstream the well, which can be exposed to major fertilizations compared to other areas nearby.

In the study area also SiO_2 shows higher concentrations during autumn. As reported in SEVERINI *et alii* (2020), SiO_2 trends and values in this area can be related to manure spreading and abundant precipitation, resulting in high concentrations in groundwater after rainier months as September and November 2019. The thick and continuous bed of fine sediments below the unconfined aquifer precludes possible contributions given by slower and deeper groundwater circuits enriched in silica. Due to the common origin of SiO_2 and NO_3^-, their spatial distribution overlaps (Fig. 7). The main difference between these two analytes lies in the slower decrease of SiO_2 concentrations among the groundwater flow path. In fact, SiO_2 does not undergo biogeochemical processes that can alter its concentrations, such as denitrification for NO_3^-. As a result, SiO_2 concentrations display a slower decrease along the groundwater flow path as compared to NO_3^-. In the left bank the denitrification process seems more effective, as NO_3^- concentrations decrease faster along the flow path than in the right bank. The higher SiO_2 and NO_3^- concentrations in the eastern area, testify the greater use of manure in this area, despite the different land use.

Among the other parameters, EC does not show a particular trend along time, except the lower values measured in September. In the eastern areas, the higher values are caused by higher concentrations of the reported analytes. Ca^{2+} concentration in soil was reported as affected by cattle manure spread (CHANG *et alii*, 1991). Thus, given the trend over time similar to SiO_2, it could be influenced by manure spread. Once again, the higher concentrations in the left bank can be related to the higher use of organic fertilizers compared to the right bank. Regarding SO_4^{2-}, mineralogical analyses performed in the same aquifer (18.5 km S-E the study area) underline the absence of sulfate in the mineralogical composition of the aquifer. As reported by other authors, it can be related to manure spreading, although in small quantities (CHANG *et alii*, 1991). In fact, in the study area their spatial distribution is like NO_3^- and SiO_2, suggesting a common origin. The temporal trend of SO_4^{2-} concentrations is closer to NO_3^- than SiO_2, as both are subjected to reduction by microbial communities. Percolating manure-rich water, under oxic conditions, can favour the accumulation of NO_3^- and SO_4^{2-} high concentrations in the upper groundwater layer. When there is no more aquifer recharge and sub-oxic conditions establish, the microbial community can use NO_3^- and then SO_4^{2-} as electron acceptors, causing their concentration decline and reduction to N_2 and H_2S, respectively. Present data do not allow to draw conclusions on the processes responsible for the trends observed, that need further studies addressing microbial communities or other proxies of dominant redox processes. Also the factor responsible for higher NO_3^-, SiO_2 and SO_4^{2-} concentrations in the left bank, possibly related to different organic fertilizer, deserves additional investigations.

FINAL OBSERVATIONS

Results from this work suggest how groundwater quality and quantity in the investigated aquifer are not only determined by specific land use and agricultural practice. In the experimental site, the eastern and western areas along the Mincio River are characterized by similar land use but with different percentages. Especially when referred to agricultural soil, this can involve different irrigation and fertilization practices. Nevertheless, on both sides of the study area, similar temporal and spatial trends of groundwater physico-chemical parameters were measured. Moreover, during the investigated period in the study area the temporal trends of NO_3^- contamination were characterized, with some wells showing higher concentrations than those set by Italian and European laws. These high NO_3^- concentrations represent a serious concern for both people and environment in the study area. In fact, the unconfined aquifer is still used in some cases for the extraction of water for human consumption. Moreover, the groundwater potentiometric map shows how the Mincio River acts as gaining river in the investigated area. This could result in the enrichment of NO_3^- in the river, boosting the eutrophication problems in the downstream Mantua lakes.

In the meantime, these findings raise new questions about the study area. How much aquifer recharge is provided in the study area is still an unanswered question. Besides, it can directly be responsible for the oxic conditions of groundwater and relatively high NO_3^- and SO_4^{2-} concentrations, making the question more relevant. Also, the differences in organic fertilizers are still relatively unknown, and they could be responsible for the differences in NO_3^- and SO_4^{2-} concentrations in the investigated area. Last but not least, it is still not known how the pivotal role of the microbial community in groundwater can shape groundwater main physico-chemical parameters. To start refining knowledge about these unanswered questions, further investigations were scheduled at the study site, fostering a multidisciplinary method that was already reported as a useful approach for the investigation of shallow aquifer systems (ZANINI *et alii*, 2018). As a consequence, multiple research will be implemented, with special regard to hydrogeological (multilevel piezometers, as in RIZZO *et alii* (2020)), isotopic (mainly stable isotopes of oxygen and deuterium, and tritium, as in PETRELLA & CELICO (2013)) and ecological methods (as in BOLPAGNI & LAINI (2016)).

ACKNOWLEDGEMENTS

We would like to thank all the private owners within the study area for allowing us to sample their wells.

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Received February 2021 - Accepted April 2021

