Herbicide and nutrient monitoring in surface waters and groundwater of a paddy district in northern Italy

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Abstract

Italy is leading rice producer in Europe and the second in the Mediterranean basin (after Egypt), with most of the production concentrated in a large paddy area between the Lombardy and Piedmont regions (northern Italy). In this area, irrigation of rice was traditionally carried out by wet seeding and continuous flooding; in the last fifteen years, this technique has been gradually replaced by dry seeding followed by a delayed flooding (DFL) or by an alternation of flooding and dry periods (FTI), which are economically more advantageous. This study presents the results of an extensive monitoring campaign designed and carried out in 2021 in a representative paddy district of the Lomellina area (Pavia, northern Italy) to assess the impact of the actual rice cropping strategies on surface water and groundwater quality, with particular attention to two widely used herbicides (MCPA and clomazone) and to nutrient losses (e.g., N, P, K). Results show that MCPA and clomazone concentrations detected in surface water and groundwater are always below the RAC (Regulatory Acceptable Concentration) values. As to nutrients, they do not show significant trends along the season in surface water and groundwater: this may be due to the fact that nutrient sources are many. Concerning the concentrations, nitrates may pose a problem for the area, especially for groundwater. However, further studies would be needed to understand to which extent rice cropping can be considered the major source of contamination for water resources.

1. Introduction

Rice is one of the most important grain crops around the world, serving as a staple food for 50% of the world population (Weng et al., 2019; Muthayya et al., 2015). Therefore, it is considered to be a high-value crop (Gosetti et al., 2019). In Europe and Northern Africa, it is cultivated on a total area of about 1.2 million hectares (FAOSTAT, 2020). In this area, the most important rice-producing countries are Egypt (554,205 ha), Italy (227,320 ha), and Spain (102,060 ha). Apart from a few dry periods needed for agronomic reasons, rice is traditionally grown in fields that are flooded from crop establishment to a few weeks before harvest. Northern Italy has a very long tradition of flooded rice, because of the high availability of water from spring precipitations and mountain runoff (Monaco et al., 2021). However, in recent years, especially during the last 10-15 years, the traditional water seeding and continuous flooding (WFL) has been gradually replaced by dry seeding, followed by a delayed flooding at the 3^{rd} – 4^{th} leaf (DFL) or even by a turn-based irrigation (FTI) when water for a continuous flooding after the dry seeding is not available (Gilardi et al., 2023). This shift was triggered by the fact that the dry seeding is economically more advantageous than the wet seeding, given the lower production costs due to the reduced amount of labour and energy inputs needed. In particular, there are benefits in the type of machinery used. In fact, with the wet seeding, farmers need dedicated tractors with metal wheels adapted to the rice paddies. This aggravates the overall farm management, including the movement of metal-wheeled tractors across roads. Especially in the case of fragmented farms where the movement of tractors and machinery is very burdensome, dry seeding guarantees a more efficient and inexpensive seeding management. In loam/sandy-loam soils (like those in the study area), dry seeding improves the effectiveness of seeding. Furthermore, dry seeding avoids the spread of algae and specific weeds (Gharsallah et al., 2023). Despite the advantages that dry seeding has brought to farmers and the water saving achievable (e.g., 14% of water saving in the whole irrigation season for DFL (Gilardi et al., 2023)), this change is leading to different unexpected problems. The main ones are: i) that the study area is facing a lowering of groundwater levels in the first months of the agricultural season. This lowering reduces the contribution of groundwater to water discharges in the irrigation network, and a shifting to June of the maximum irrigation requirement of the district, that is currently leading to a more exasperated competition between rice and the other crops cultivated in the area (Gilardi et al., 2023; Zampieri et al., 2015; Zampieri et al., 2019); ii) increase in surface and groundwater nitrogen losses: high soil solution nitrate concentrations and leaching from the root zone as a result of nitrification under oxic soil conditions represents the greatest environmental constraint of dry seeding cropping system (Miniotti et al., 2016; Pittelkow et al., 2015; Belder et al., 2005), threatening river and groundwater quality (Zampieri et al., 2019); iii) considering ecosystems, dry seeding can bring some serious disadvantages as traditionally flooded rice fields provide habitat for spring migrants and locally breeding birds (Imperio et al., 2017).

Rice production is affected by weed proliferation that may significantly reduce rice yields. To protect their crops, farmers widely use combinations of herbicides. Moreover, in order to improve yields, nutrients are also used, as fertilisers. Despite the industry makes efforts to design formulations characterised by high efficiency at low doses and low persistence in order to minimise the environmental impact, the intrinsic features of these chemicals make them able to spread in water and soil, as well as in the atmosphere. Therefore, the assessment of their environmental impact is of great importance. According to Gosetti et al. (2019), the contamination of water bodies is one of the major problems related to the sustainability of the areas cultivated with rice.

From a legislative viewpoint, the protection of water resources from contamination due to pesticide use is one of the main goals of the European policy (e.g., 2000/60/EC, 2008/105/EC, 2009/128/EC), as well as the environmental quality of freshwater with respect to eutrophication and nutrient concentrations (e.g., 91/676/EEC, 91/271/EEC, 2010/75/EU, 2020/2184/EU for drinking water, and the before-mentioned 2000/60/EC). Different criteria have been established to reduce pesticide transfers from sites of application to water resources (Vidotto et al., 2021). Moreover, agri-environmental measures have been developed and applied to reduce nutrient pollution of the aquatic environment (e.g., Common Agricultural Policy, European Green Deal, 'Farm to Fork' Strategy). Different studies showed that herbicides and their metabolites are the Plant Protection Products (PPPs) mostly detected in surface waters, while fungicides were the substances mainly found in groundwater (Parisse et al., 2020). The intensive use of PPPs may pose a risk to the environment and this risk is enhanced when they are applied on rice, due to the strict connection with the water compartment (Resgalla et al., 2007; Ueji and Inao, 2008). The 2020 report made by the Italian National Institute for Environment Protection and Research (ISPRA) showed PPP residues on 77.3% and 35.9% of the monitored points in surface waters and groundwater, respectively (Parisse et al., 2020; Vidotto et al., 2021).

While the impact of rice cropping on the water resource in Asia is relatively well-studied (Liu et al., 2018; Cui et al., 2020; Weng et al., 2019; Harlina et al., 2014), there is less research devoted to this topic in Europe and, in particular, in Italy (Gosetti et al., 2019; and Miniotti et al., 2016, only for nitrogen). The present study was developed in the context of the MEDWATERICE project (www.medwaterice.org), an international project that aimed to explore sustainability of innovative irrigation options, to reduce rice water consumption and rice environmental impacts, and to extend rice cultivation outside of the traditional paddy areas. The project included a number of case studies in different Mediterranean countries. The Italian case study was focussed on enhancing the understanding of water quantity and environmental issues in the rice cropping systems of the largest rice area in Europe, facing these problems both at the farm scale and at the district scale. In particular, the irrigation district scale (10^3-10^4 hectares) is crucial when the goal is to support decisions of authorities that deal with water resource planning and management at the regional scale, since rice fields are often not isolated units but part of large areas where strong intra-field interactions may occur. The pilot district for the study is located in San Giorgio di Lomellina (Pavia, Italy) and the research aims to evaluate the impact on surface water and groundwater quality of rice cropping in northern Italy, of which the study district is considered to be a representative area. Being rice the crop with the largest impact in terms of fertilisers and pesticide use (Bechini and Castoldi, 2009; Zampieri et al., 2019), this study has the purpose of illustrating the results of a monitoring campaign conducted in 2021 to assess the impact on surface water and groundwater of MCPA and clomazone, two active ingredients widely used on rice, and of nutrients (i.e., N, P, K) in the San Giorgio di Lomellina district. In recent years, the usage of MCPA and clomazone in the cultivation of rice in northern Italy has increased, and therefore these herbicides are gaining attention as far as their environmental fate is concerned. However, to our knowledge some research is available (Fernández et al., 2019; López-Piñeiro et al., 2019; McManus et al., 2014; Galhano et al., 2011; Alister et al., 2010; Marchesan et al., 2007), but not for Italy nor specifically for the district-scale. MCPA (2-methyl-4-chlorophenoxyacetic acid) is a systemic post-emergence phenoxy herbicide used to control broadleaf annual and perennial weeds (including thistle and dock) in rice, cereals, vines, peas, potatoes, flax, grasslands, forestry applications, and on rights-of-way (Richard and Pohanish, 2015). Due to its high solubility and poor adsorption to the soil matrix, MCPA is susceptible to transport into surface and groundwater bodies. For this reason, it can be responsible of compromised water quality and breaches of legislative standards (Morton et al., 2020). In the study area, MCPA is used during sprouting on rice, approximately 35 to 45 days after seeding. However, products based on MCPA exist, which are also registered for other uses, for example maize, other cereals (e.g., barley, sorghum, oats, wheat), canal/ditch banks, railways, industrial areas. Clomazone selectively controls many annual broadleaved and grass weeds in different crops (e.g., rice, sugarcane, tobacco, soybean, cotton, peppers, and pumpkin). It can be applied pre-emergence or pre-planting with incorporation, but has limited post-emergence activity (Zimdahl, 2018). It is highly soluble in water and quite volatile, so may be prone to drift. It is not persistent in the soil system, but may be persistent under certain conditions in waterbodies. It tends to be moderately toxic to most fauna and flora. It is moderately toxic to mammals and is considered to be a reproduction/developmental toxin (PPDB: Pesticide Properties DataBase; http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/168.htm). In the study area, it is applied on rice on dry soil, at the stage of 2-3 leaves, 20 to 30 days after seeding. Rice is seeded in the area between the end of April and the end of May.

As to nutrients, this study focused on N, P and K losses. N, P, and K are essential nutrients for plant growing and an excess can stimulate nuisance growths of aquatic plants in water bodies. The most common forms of N available for plant growth in water are the inorganic forms, namely, nitrate (NO_3), nitrite (NO_2) and ammonia (NH_3/NH_4) and organic forms such as urea (the breakdown product of proteins). Nitrate is the most commonly available and ammonia the most readily assimilated by plants.

2. Materials and methods

2.1. Case study area

The study area presented in this paper is located in the most important rice-growing area of Italy, that is the portion of the Padana plain on the left bank of the Po River and along the Ticino River, straddling the regions of Lombardy and Piedmont (more than 200,000 ha; about 92% of the Italian rice-growing area). The pilot irrigation district for the MEDWATERICE project is within the administrative boundary of San Giorgio di Lomellina (Pavia), located about 45 km southwest of the city of Milan and extending over an area of 990 ha. It is bounded to the West by the river Agogna and to the East by the river Erbognone (or Arbogna) (Figure 1). This district is considered to be representative of a large part of Italy's main rice-growing area.

Over the last decade, the rice area within the district remained stable at 90% of the agricultural land. The remaining 10% is mainly cropped with maize and poplar. Soils are generally sandy-loam or loamy-sand. Because of the texture, soil organic matter content is low as well as nitrogen content. The climate is humid subtropical. From a geomorphological point of view, the district area belongs to the lower part of the alluvial plain originated during the Würm glaciation (Mayer et al., 2019). The surface area is mainly flat, except for some sand deposits of fluvial origin and the valleys where the main rivers flow nowadays. The phreatic groundwater surface varies and can be very shallow in some areas due to the topography and the summer flooding of paddies (Mayer et al., 2019; Gilardi et al., 2023). Associazione Irrigazione Est Sesia (AIES) is responsible of the management of the irrigation and drainage network in the district. Irrigation water comes almost exclusively from surface water bodies (Arbogna and Po rivers through the Cavour canal). The main irrigation channels for the district are: 'Canalino', 'Cavo Isimbardi' and 'Roggia Comunale di San Giorgio'. As well as in the other Italian rice areas, Ente Nazionale Risi (ENR) is informed of the agronomic practices adopted by farmers.

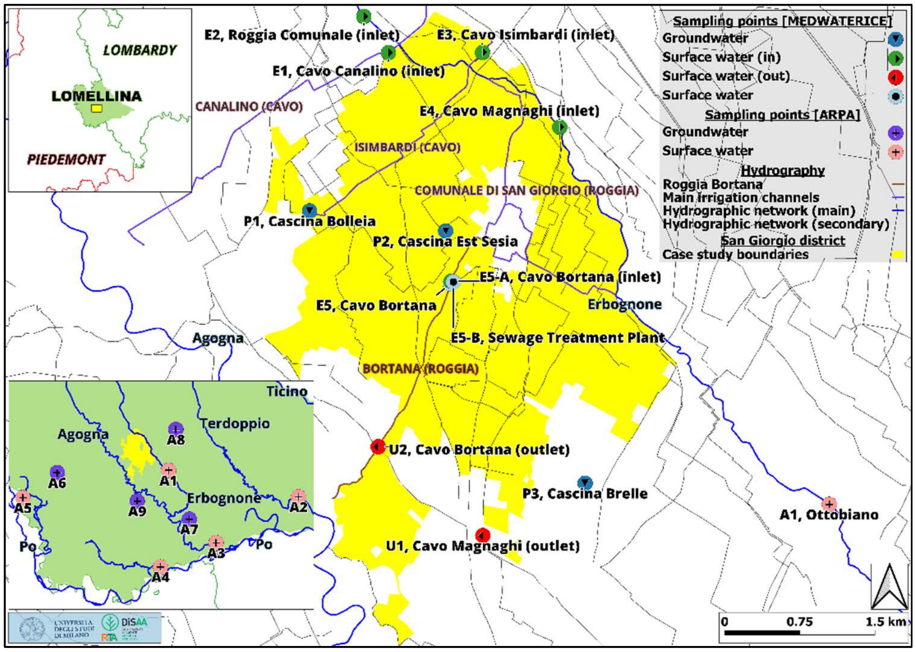


Fig. 1 General overview of the San Giorgio irrigation district (Pavia, Italy). Case study area in yellow

In recent years, the San Giorgio di Lomellina irrigation district has witnessed a massive adoption of the dry seeding technique, followed by a DFL or by a FTI, instead of the traditional WFL. Table 1 illustrates the transition from the wet to the dry seeding practices in the San Giorgio di Lomellina district during the period 2013-2019, in which DFL reached 100% of the total rice area.

Table 1 Transition from the wet to the dry seeding practices in the San Giorgio di Lomellina district during the period 2013-2019 (ENR data, 2020)

Agricultural season	Dry seeding (%)	Wet seeding (%)
2013	40.1	59.9
2016	92.5	7.5
2019	100.0	0.0

2.2. Monitoring campaign

As to groundwater, three piezometers were identified. The selection was based on groundwater flow direction and on groundwater level (Figure 2), with two piezometers located in the shallow and one in the deep groundwater areas (Figure 2). Piezometric wells were positioned in the district at the beginning of 2015, and are made by PVC pipes (from 3 to 4.5 m long, 1.5 m windowed in the lower part, with an internal diameter of about 4 cm) installed into holes drilled with a hand auger. During this study, they were sampled approximately on a monthly basis.

For surface water, water was sampled at the inlet and at the outlet of the district in order to see whether herbicide usage and fertilisation within the district had an impact on water quality. Hence, a choice was made to sample the main canals entering the district and draining the district, and the following were selected: Roggia Comunale, Cavo Canalino, Cavo Isimbardi, Roggia Bortana, and Cavo Magnaghi. In particular: five irrigation inlet points, two irrigation outlet points, and one point in a channel collecting also water from a civil sewage treatment plant (STP) were identified (Figure 1). The latter was selected in order to assess the impact of non-agricultural sources, especially in relation to N. Figure 3 reports details relative to the sampling points in the confluence of the ditch from the STP and Roggia Bortana. Roggia Bortana was sampled upstream (E5-A) and downstream (E5) the ditch from the STP. The ditch from the STP was sampled from a bridge located approximately 20 m from the confluence with Roggia Bortana (E5-B).

A number of criteria were used to choose the surface water sampling points: importance in the irrigation network, accessibility for sampling, presence of water discharge, location at the inlet/outlet of the district (to compare quality of water entering and going out of the district).

The sampling campaign started on 26th May 2021 and continued until the end of the agricultural season (3rd September 2021), including eleven sampling events (Table 2). In addition, a sampling event was performed on 20th April to assess water quality prior to pesticide and fertiliser treatments on rice (t_0 sampling event). Piezometric wells were often dry out of the flooding periods, which is consistent with the irrigation management strategies (i.e., dry seeding and delayed flooding or dry seeding and fixed turned flooding) adopted in the area in the last fifteen years, which triggered a decrease in groundwater levels until June.

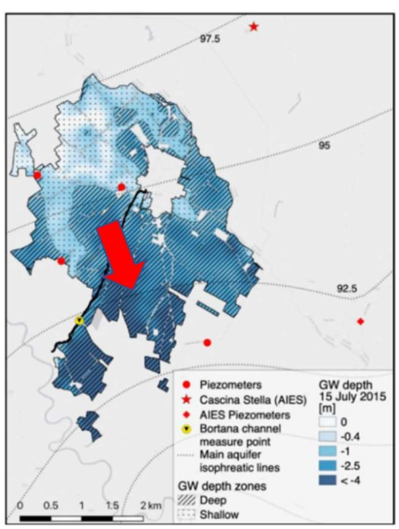


Fig. 2 Groundwater depth zones in San Giorgio (2015) and main groundwater flux direction (red arrow)

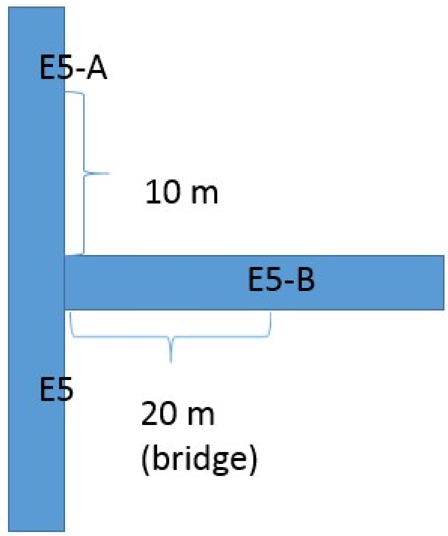


Fig. 3 Sketch of the E5 sampling points. E5-A is Roggia Bortana upstream the ditch from the sewage treatment plant (STP). E5 is Roggia Bortana downstream the ditch from the STP and E5-B is the ditch from the STP. E5-B was sampled from a bridge located approximately 20 m from the confluence with Roggia Bortana

Table 2 Details about the monitoring campaign (OK = sample collected; X = sample not collected)

	Event 1	Event 2	Event 3	Event 4	Event 5	Event 6	Event 7	Event 8	Event 9	Event 10	Event 11	Event 12
Date	20/4/21	26/5/21	3/6/21	10/6/21	17/6/21	23/6/21	1/7/21	8/7/21	15/7/21	29/7/21	19/8/21	3/9/21
E1	X	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E2	OK*	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E3	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E4	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E5	X	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E5-A	X	X	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
E5-B	X	X	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
U2	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
U1	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
P1	X	X	X	X	OK	X	X	X	OK	X	OK	X
P2	X	X	OK	X	OK	X	X	X	OK	X	OK	X
P3	X	X	X	X	OK**	X	X	X	OK	X	OK	X

*sample collected in the Agogna river (just upstream the diversion of Roggia Comunale); **sample partially collected (only 1 Nalgene flask and 1 Falcon tube)

2.3. Sampling procedure

Water sampling was carried out in the best possible way to preserve test compounds from photodegradation and from surface adsorption on sample containers (e.g., use of fluorinated HDPE flasks, samples protection from sunlight).

Surface water sampling consisted in a series of grab samples. In each sampling point, three samples of 250 mL each were taken at one-hour intervals. A composite sample of 750 mL was then created, merging the three samples. The composite sample was used to prepare three Nalgene flasks of 200 mL and a 50-mL Falcone tube for the different analyses.

As to groundwater, all sampling procedures were taken from existing guidelines (GCPF, 2001, and Gimsing et al., 2019) to ensure a contamination-free and representative sample of the local groundwater. In particular, the piezometer head was cleaned with water/acetone before opening the seals and a plastic film was laid on the soil to avoid contamination of the equipment. A sampling pipe connected to a 12V vacuum peristaltic pump was inserted and lowered to the bottom of the piezometer. All components used were made from inert materials. This ensured that the samples taken are neither influenced nor altered by the sampling procedure. Before collecting samples, piezometer was purged. Purging involves the removal of three times the water volume inside the piezometer in order to minimize a potential risk of contamination/alteration of the samples. Two sample replicates were collected in labelled 250 ml fluorinated HDPE-bottles and an additional sample was collected in labelled 60 ml plastic container. After collecting the samples, the tube and the glassware were rinsed with water and acetone in order to prevent cross contamination between piezometers. Immediately after collection, both surface water and groundwater samples were stored in a cool dark box or portable freezer. The temperature was kept below -8°C until transferred to frozen storage (-20 ºC +/- 5°C). During transport, the samples were kept at a low temperature using portable freezers (at least -8°C +/- 2°C) and then stored in the freezer.

2.4. Analytical methods

Nutrients from the water samples were all analysed via a spectrophotometric method with a Hach kit associated with a Hach Lange DR6000 spectrophotometer: K (LCK228, 5 – 50 mg/L, Hach), NO_3 (LCK339, 0.23 – 13.5 mg/L, Hach), NH_3/NH_4 (LCK304, 0.015 – 2.0 mg/L, Hach) and P (LCK349, 0.05 – 1.5 mg/L, Hach). Differently, NO_2 (N-NO_2 0.09 – 0.5 mg/L) was analysed using a modified version of the colorimetric method known as Griess method. The method is based on the reaction of nitrite with sulphanilamide (Sigma-Aldrich) in the presence of hydrochloric acid (36%, Carlo Erba) to form a diazonium cation, which is subsequently coupled with N-(1-naphthyl)ethylenediamine dihydrochloride (Sigma-Aldrich) in acidic medium to form a stable bluish violet azo dye that absorbs at 530 nm. Urea was analysed with a Urea Assay Kit from Sigma-Aldrich (N-Ureic 0.56 – 2.8 mg/L). Total nitrogen was estimated as the sum of inorganic nitrogen forms (i.e., nitrates, nitrites, ammonia) and organic nitrogen form (i.e., urea). Urea was used as main component of organic nitrogen due to the fact that urea-based fertilisers account as one of the main sources of organic nitrogen in paddy fields (Han et al., 2021).

As to herbicides, Clomazone (Supelco, PESTANAL®, analytical standard) and MCPA (Honeywell Riedel-de-Haën) were separated with a RP-18 column (150x2.1 mm, Kinetex 5 um Phenomenex) and quantified by high performance liquid chromatography (HPLC) with triple quadrupole mass detector. The mobile phase consisted of methanol:water acidified with 0.2% formic acid and with a gradient programme applied from 25:75% v/v to 65:35% v/v in 6 min and isocratic for 8 min. Flow rate was 0.2 mL/min and the injection volume was 20 µL. The ionization was carried out with an ESI interface (Thermo-Fisher) in positive mode for clomazone and negative mode for MCPA. Parameters were: spray capillary voltage 4,200 V for clomazone and 3,500 for MCPA, sheath gas and auxiliary gas 35 and 14 psi, respectively; temperature of the heated capillary 350° C, source collision induced dissociation (CID) 10 V. The mass spectrometric analysis was performed in selected reaction monitoring (SRM) mode. For the fragmentation of clomazone, $[M]^+ = 240$ m/z, the argon collision pressure was 1.2 mTorr and the detected and quantified ions were 89, 99 m/z (collision energy 45 V) and 125 m/z (20 V). For the detected and quantified ions of MCPA, $[M]^- = 199$ m/z, the argon collision pressure was 1.2 mTorr and the fragment ions were 106 m/z (collision energy 30 V) and 141 m/z (15 V).

Oasis HLB cartridges (Supelco, Supel™-Select HLB SPE Tube) were considered suitable SPE devices for pre-concentration of the herbicides in this study due to their hydrophilic and lipophilic characteristics as reported in Tran et al. (2007). Briefly, samples pH was decreased to 3 with formic acid (Sigma-Aldrich) and NaCl (Sigma-Aldrich, 10 g/L) was added to aid in the recoveries. Before pre-concentration, all samples were filtered through Glass microfiber filters (Gf/A, Whatman). The water samples were then loaded onto the cartridges via a vacuum manifold and after completion the cartridges were washed with deionized water. The excess water was removed by opening the valves and letting air to pass through the cartridge for 30 min. The herbicides absorbed on the cartridges were eluted with methanol (Carlo Erba) and after reducing to near dryness under a nitrogen stream, the samples were reconstituted in a mixture of the HPLC mobile phase (Methanol/HPLC grade Water 1:1) and an aliquot of 20 µL was then injected into the HPLC system. Overall, this extraction procedure resulted in a 1:1000 pre-concentration of water samples prior to HPLC-MS analysis.

Calibration curves were constructed from the analysis of solutions containing the range of 0.1 – 1000 µg/L of each analyte, showing a good linearity and a LOQ (Limit of Quantification) (based upon a signal to noise ratio of 10:1) of 4 µg/L for both herbicides (0.004 µg/L considering not preconcentrated samples). Recoveries from spiked herbicides in both tap and distilled water varied from 80 to 100% for clomazone and 85 to 100% for MCPA.

Statistical analysis of nutrient and herbicide concentrations in surface water and groundwater samples was evaluated using a Kruskal-Wallis coupled with Dunn-Bonferroni test with RStudio 4.4.0 software. Herbicide and nutrient concentration mean values were calculated by replacing "<LOQ" with a value equal to "LOQ/2".

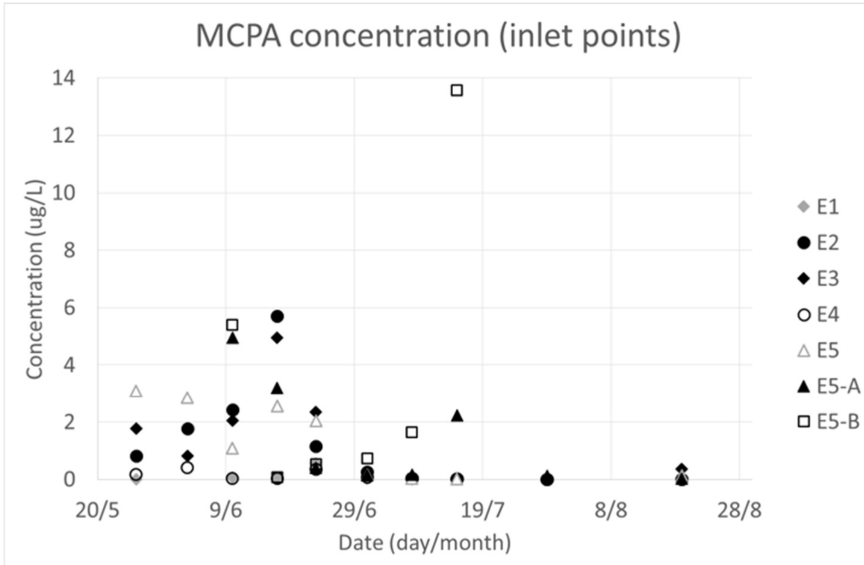
3.Results and discussion

3.1. Herbicides in surface water

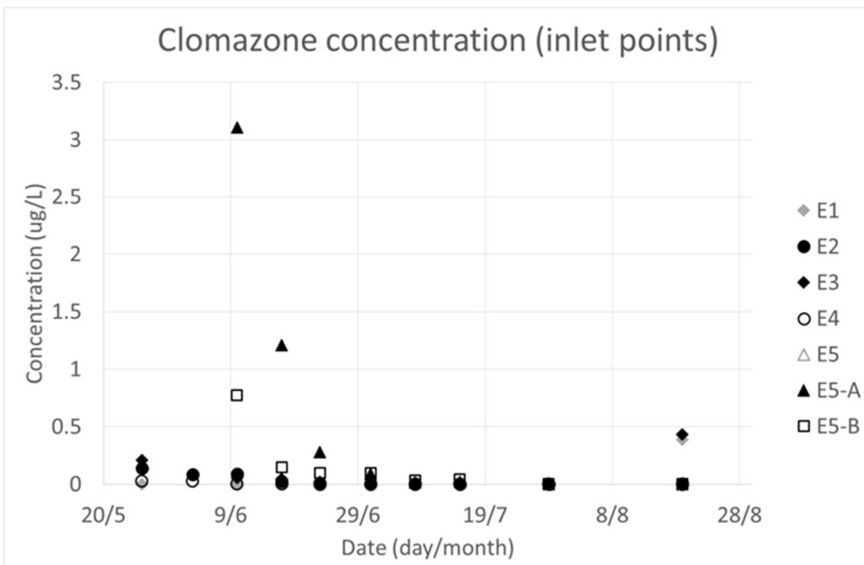
The monitored clomazone and MCPA concentrations show that water quality at the inlet of the district is affected by treatments occurring outside the district. Concentrations detected are always below the RAC values for both herbicides. In general, the average concentrations monitored at the inlet and at the outlet of the district are comparable, so we can infer that the herbicide treatments occurred within the district do not worsen water quality.

In the case of MCPA, the minimum concentration detected in the inlet sampling points is <LOQ, the maximum is 13.56 µg/L and the mean value is 1.13 µg/L. Excluding the highest peak dated 15th July, concentrations tend to be higher in June (10th and 17th June) than in the rest of the period monitored. If the seeding occurred in the district around the end of April or the beginning of May this would be consistent with the timing of treatment on rice. The highest peak was monitored in the E5-B sampling point. This point is located in the ditch coming from the STP, so we can hypothesise that it is not triggered by MCPA treatment on rice (Figure 3). It can be noted that this high peak does not affect the concentration monitored in the E5 sampling point, downstream the STP. Discharge from the STP was estimated lower (0.18 m^3/s) than the discharge at E5 (0.28 m^3/s), however, MCPA concentration downstream the STP is even lower than upstream. We hypothesise that this is an outlier, maybe due to human error in the sampling or in the labelling.

For clomazone (Figure 4b), the minimum concentration monitored is <LOQ, the maximum is 3.11 µg/L and the mean value is 0.17 µg/L. Also in this case, there is a trend with higher concentrations in June, consistently with the seeding and treatment timing in the study area.



(a)



(b)

Fig. 4 MCPA (a) and clomazone (b) concentrations in the inlet sampling points

At the outlet of the district (Figure 5), MCPA minimum concentration detected is <LOQ, the maximum is 3.31 µg/L, and the mean value is 0.48 µg/L. Especially in U2, it is possible to note a trend with higher concentrations in June, which then decrease, and then slightly increase again at the end of August (Figure 5a). A similar trend can be observed for clomazone (Figure 5b). Clomazone minimum concentration monitored is <LOQ, the maximum is 0.36 µg/L, and the mean value is 0.04 µg/L.

The monitored clomazone and MCPA concentrations show that the water quality at the inlet of the district is affected by treatments occurring outside (i.e., upstream) the district. In some cases, concentrations are below 1 µg/L (e.g., E1, E4); in other cases, concentrations are higher (e.g., E2, E3, E5). However, MCPA and clomazone concentrations detected are always below the RAC values, which are 5.3 µg/L for clomazone (chronic risk for aquatic invertebrates) (EC, 2017), and 15.2 µg/L for MCPA (acute risk for aquatic plants) (CTGB, 2017). At the outlet, herbicide concentrations tend to be higher in U2 than in U1, for both MCPA and clomazone. However, they are always below the RAC values. Therefore it is believed that there is little impact on water quality and that the agronomic practices are suitable and well applied to minimise the environmental risk related to these two herbicides. In general, the average concentrations monitored at the inlet and at the outlet of the district are comparable: in fact, the statistical analysis performed did not show a significant difference among the sampling points. So we can infer that the herbicide treatments occurred within the district do not worsen water quality.

When looking at other studies, MCPA was detected in Swiss surface waters to a maximum concentration of 1.6 µg/L in five agricultural catchments (Spycher et al., 2018). In the present study concentrations may be higher due to a more widespread application and to the specificities of rice cropping. In Ireland, data collected during the period 2013–2015 show MCPA maximum concentration of 18 µg/L, recorded in 2013 in the Banoge River (Co. Wexford) (EPA, 2017; Morton, 2020). For clomazone, Marchesan et al. (2007) reported average concentrations ranging between 1.34 µg/L and 4.97 µg/L and maximum concentrations of 4.82-8.85 µg/L in two Brazilian rivers during the rice-growing season.

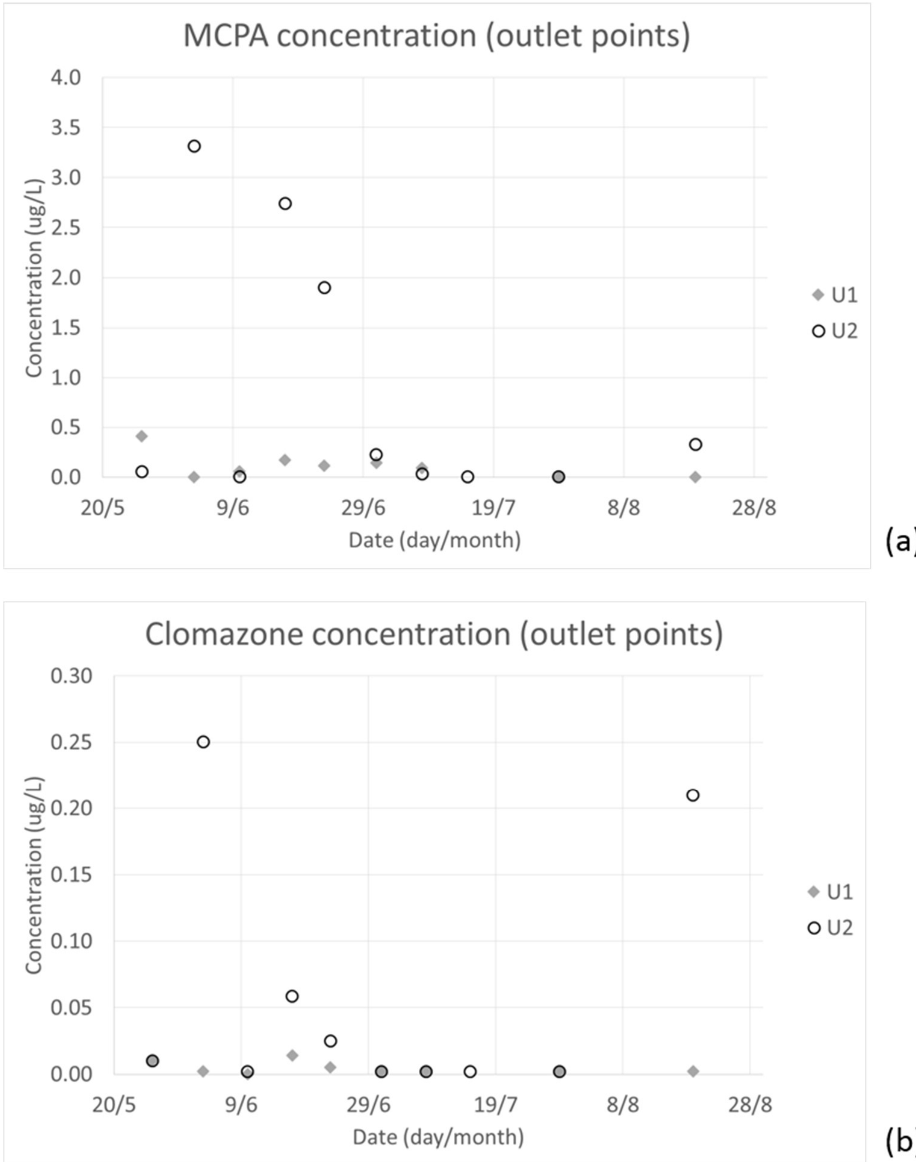


Fig. 5 MCPA (a) and clomazone (b) concentrations in the outlet sampling points

The regional agency for environmental protection (ARPA, Agenzia Regionale per la Protezione dell'Ambiente) of the Lombardy Region regularly monitors water quality in the regional territory. For surface water, in the period 2016-2021 data were monitored with different frequency and timing, depending on year and location. For clomazone, data by ARPA are available only for 2019 to 2021. ARPA data in the period 2016-2021 in the neighbourhood of the study area (i.e., Breme, Pieve del Cairo, Mezzana Bigli, Zinasco and Ottobiano sampling points) show maximum concentrations in surface water that are lower than those found in the present study, which were 5.7 µg/L for MCPA (13.56 µg/L in the ditch from the STP) and 3.1 µg/L for clomazone. For MCPA, ARPA average concentration is 0.54 µg/L (min <0.03 µg/L – max 0.74 µg/L) in June, 0.09 µg/L (min <0.03 µg/L – max

0.14 µg/L) in July, and 0.01 µg/L in August (min <0.03 µg/L – max 0.03 µg/L). For clomazone, ARPA average concentration is 0.08 µg/L (min <0.03 µg/L – max 0.25 µg/L) in June, 0.01 µg/L (min <0.03 µg/L – max 0.06 µg/L) in July, and in August all concentration values in the dataset are <0.03 µg/L. The differences between ARPA data and the data of this study could be due to the fact that ARPA monitoring was not continuous along the whole agricultural season. In particular, in the agricultural season June-August 2021, ARPA monitored surface water only once (in June or July, depending on the sampling point); however, with a single sampling event it is difficult to detect herbicide peaks. Moreover, in our sampling discrepancies in concentrations are observed among monitoring points, suggesting that the sampling location (due to its site-specific conditions) can have an important impact on the levels of pesticides in surface water. Finally, ARPA sampling points are commonly located in larger streams and channels farer from the paddy fields compared to those selected in the present study (which leads to a different role of dilution). Indeed, in the present study, surface water samples are always taken from small water bodies close to rice areas.

3.2. Nutrients in surface water

In the case of nutrients in surface water, the main highlights are: (i) no trend is observed and nutrient losses are spread along the whole agricultural season; (ii) nitrate concentrations tend to be higher at the outlet than at the inlet; (iii) a K peak of almost 60 mg/L is observed at the outlet and may be linked to a heavy rainfall event.

No specific trends can be observed at the different sampling points, which reasonably means that nutrient losses to surface water tend to be spread along the whole agricultural season (Figure 6). Note that N losses can be due to both extensive use of N-based fertilisers, livestock (Bijay-Singh and Craswell, 2021), but also to civil wastewater discharges and industrial activities. According to Mockler et al. (2017), N contributions from wastewater ranged between ≤7% and 33%, while P contributions reached 78% in the most densely populated areas.

In the case of the inlet sampling points, for total N, the minimum concentration detected in the inlet sampling points is 0.32 mg/L, the maximum is 7.82 mg/L and the mean value is 2.10 mg/L. For P-PO_4, the minimum concentration monitored is <LOQ mg/L, the maximum is 3.88 mg/L and the mean value is 0.34 mg/L. As shown in Figure 6b, a single peak was detected on 29th July (3.88 mg/L in E2). This peak may have been triggered by a heavy rainfall event occurred on the night between 26th and 27th July (21 mm in an hour). In the case of K, the minimum concentration monitored is <LOQ, the maximum is 9.90 mg/L and the mean value is 3.58 mg/L. The ditch from the STP (E5-B; Figure 3) shows the highest average concentration of total N (3.32 mg/L). However, in terms of minimum and

maximum concentrations, values are in line with other sampling points. Pryor et al. (2007) reported higher total N average concentrations from different STPs in Narragansett Bay (USA), ranging between 7.5 mg/L and 69 mg/L. Note that the limit imposed by the Italian legislation (reported by the 'Gazzetta Ufficiale della Repubblica Italiana' – serie generale n.88, Allegato 5, 2006) is either a yearly average concentration of 10 mg/L or a daily average concentration of 20 mg/L. The average P-PO_4 concentration measured in E5-B (0.63 mg/L) is comparable with the average detected in other points. The maximum concentration in E5-B is 1.43 mg/L and it is in line with the lower limit of the data published by Cabo et al. (2022), who reported a phosphate concentration in the range 1.5–3 mg/L of P-PO_4 in the final discharge effluent from a STP in Spain. The limit imposed by the Italian legislation (reported by the 'Gazzetta Ufficiale della Repubblica Italiana' – serie generale n.88, Allegato 5, 2006) is 10 mg/L of total P. For K, E5-B shows the highest mean value (5.49 mg/L). Maximum concentration in E5-B (9.02 mg/L) is comparable with other sampling points. Minimum concentration is <LOQ. K concentration in effluents from domestic wastewater reported by Arienzo et al. (2009) vary between 10 and 30 mg/L. Data collected in the present study tend to be lower, as the maximum value is in line with the lower limit of this range. By comparing concentrations of total N, P-PO_4 and K in E5-A (upstream the STP) and in E5 (downstream the STP), we see that concentrations are higher downstream the STP in the 80% and 90% of the samples, for total N and P-PO_4 respectively. In the case of K, concentrations are higher downstream only in the 40% of the samples.

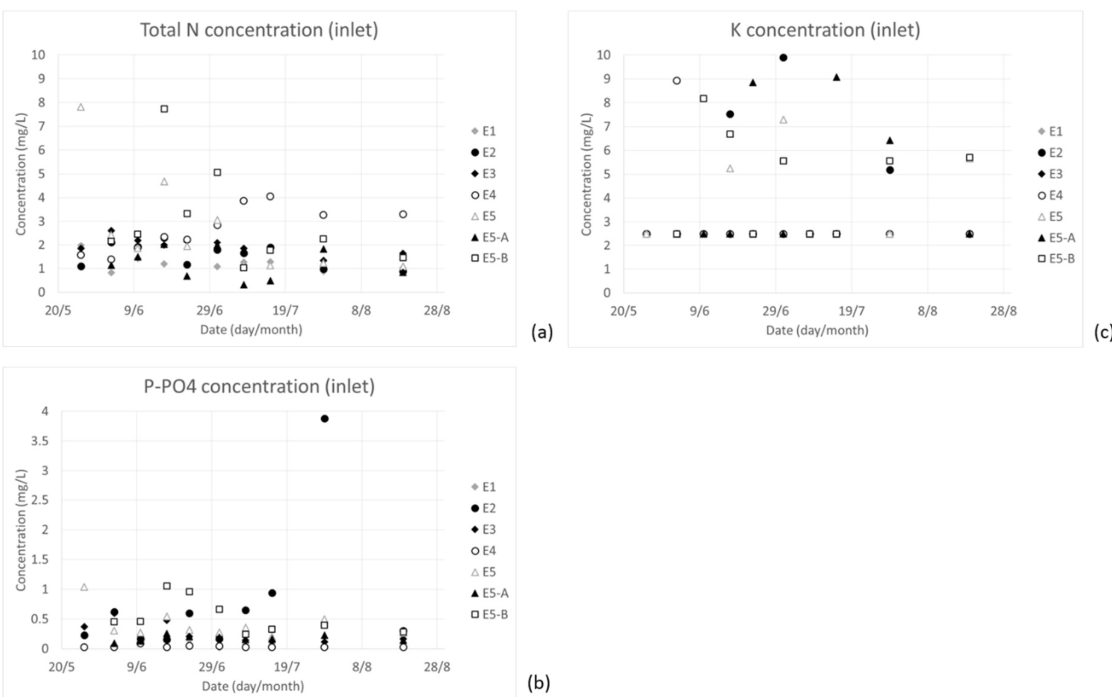


Fig. 6 Nutrient concentrations detected at the inlet sampling points: total N (a), P-PO_4 (b), and K (c)

At the outlet, total N minimum concentration is 1.25 mg/L, the maximum is 3.59 mg/L and the mean value is 2.33 mg/L. P-PO_4 minimum concentration is <LOQ, the maximum is 0.66 mg/L and the mean value is 0.24 mg/L. K minimum concentration detected is <LOQ, the maximum is 57.60 mg/L, and the mean value is 5.30 mg/L. It is important to note that, over 24 samples (12 sampling events times 2 outlet sampling points), in 20 of them, K concentration was <LOQ, in three of them it was 6-7 mg/L and in the remaining sample the concentration detected was 57.60 mg/L (Figure 7). This high peak can be linked to the heavy rainfall event mentioned before, considering that K can be easily lost by the leaching process (da C. Mendes, 2016).

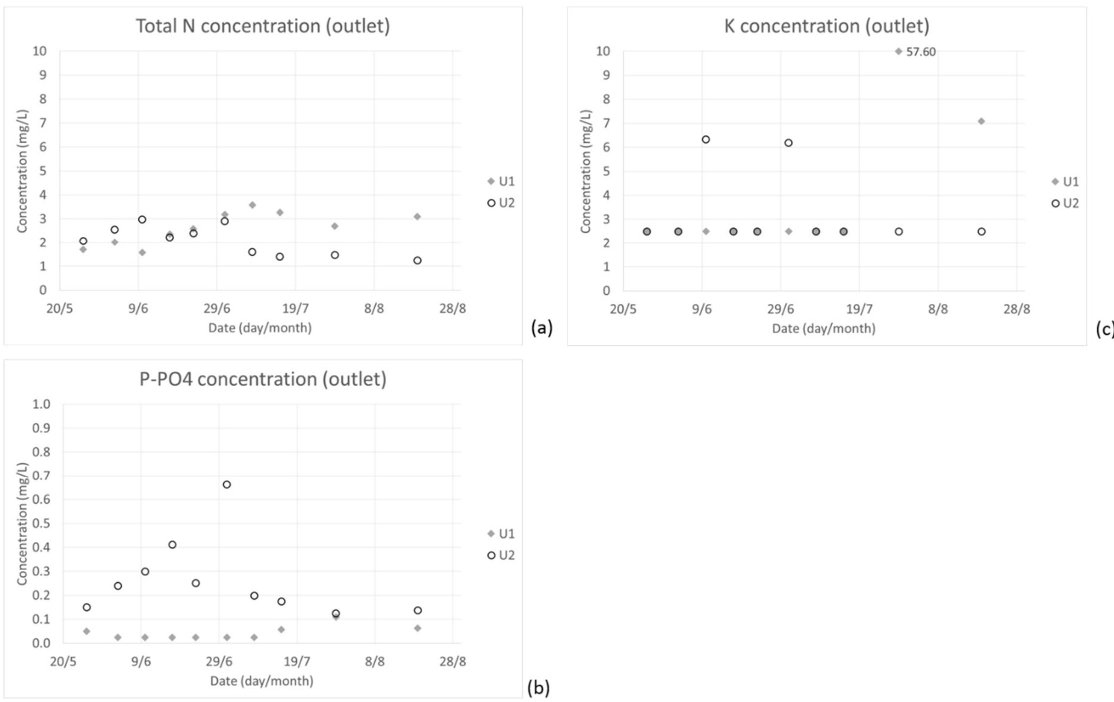


Fig. 7 Nutrient concentrations detected at the outlet sampling points: Total N (a), P-PO_4 (b), and K (c)

By comparing data monitored at the inlet of the district with data monitored at the outlet, it can be seen that total N maximum concentration is 7.82 mg/L at the inlet and 3.59 mg/L at the outlet; while mean concentrations are 2.10 mg/L at the inlet and 2.33 mg/L at the outlet. For P-PO_4, maximum and mean values are higher at the inlet (3.88 and 0.34 mg/L respectively) than at the outlet (0.66 and 0.24 mg/L respectively). In the case of K, concentrations at the outlet are higher than at the inlet: maximum concentrations are 9.90 mg/L and 57.60 mg/L at the inlet and outlet respectively. K mean values are 3.58 mg/L at the inlet and 5.30 mg/L at the outlet.

The statistical analysis performed showed that, when comparing surface water sampling points, the main significant difference in the monitoring period for N concentrations was observed between E1 and both U1 and U2. E1 exhibited significantly lower N concentrations compared to U1 and U2 (data not shown). This difference was not observed for other inlet sampling points, while a statistically significant difference was observed for E1 and both E4 and E5-B. The only significant difference in the monitoring period for K concentrations was observed between E5-B and both E1 and E3, with E5-B having lower K compared to both E1 and E3 (data not shown). P concentrations showed the highest variation. Significant differences were observed between several inlet sampling points (E1 – E2, E2 – E4, E3 – E4, E1 – E5, E4 – E5, E1 – E5-B and E4 – E5-B), and between U1 and various other sampling points (E2, E3, E5, E5-B), with U1 concentrations lower than the inlet sampling points (data not shown). So, there seems to be an increase in N concentrations and a decrease in P concentrations within the district.

When looking at N-NO_3 only, at the inlet, minimum, maximum and average concentrations of N-NO_3 are 0.25 mg/L, 3.73 mg/L, and 1.12 mg/L respectively. At the outlet, minimum concentration is 0.73 mg/L, maximum concentration is 3.32 and the mean value is 1.71 mg/L. Miniotti et al. (2016) reported field-scale data collected in 2012-2013, where N-NO_3 concentrations reached a maximum concentration of 5.50 mg/L. Amin et al. (2021) reported N-NO_3 concentrations in surface water from a rice field, where a range of 0.6–5.6 mg/L was monitored. N-NO_3 concentrations detected in the present study are in line with the values reported by Miniotti (2016) and Amin (2021). According to a synthetic index for NO_3 developed by ISPRA, the Italian Institute for Environmental Protection and Research (ISPRA, 2023) and based on 91/676/CEE Directive, as far as nitrates are concerned, the following thresholds are established to characterize NO_3 status in surface waters:

- 0-9.99 mg/L
- 10-24.99 mg/L (significance threshold)
- 25-39.99 mg/L (high significance threshold)
- 40-50 mg/L (attention threshold)
- >50 mg/L (pollution threshold)

At the inlet of the district, nitrate concentrations fall in the ‘significance’ (10-24.99 mg/L) class in 6.4% of the samples. At the outlet, they fall in the range of ‘significance’ in 25% of them. At both inlet and outlet, concentrations are never in the higher classes.

Data monitored by ARPA in the period 2016-2021 show maximum concentrations that tend to be lower than the data observed in this study, which are 7.82 mg/L for total N, 3.88 mg/L for P-PO_4 and 57.60 mg/L for K. For total N, ARPA average concentration is 2.33 mg/L (min 1.2 mg/L – max 3.7 mg/L) in June, 1.94 mg/L (min <1.3 mg/L – max 2.5 mg/L) in July, and 1.93 mg/L in August (min 1.1 mg/L – max 3.8 mg/L). For total P, ARPA average concentration is 0.06 mg/L (min <0.05 mg/L – max 0.1 mg/L) in June, 0.05 mg/L (min <0.05 mg/L – max 0.12 mg/L) in July, and 0.07 mg/L (min 0.05 mg/L – max 0.1 mg/L) in August. For K, ARPA average concentration is 3.26 mg/L (min 2.5 mg/L – max 4.3 mg/L) in June, 3.18 mg/L (min 2.7 mg/L – max 3.8 mg/L) in July, and 3.37 mg/L (min 2.9 mg/L – max 4.1 mg/L) in August. The reasons for the lower values found by ARPA are the same as those already mentioned for herbicides.

3.3. Herbicides in groundwater

In this section groundwater quality results are reported and discussed. The main highlight is that herbicide concentrations detected in the samples are always below 0.02 μg/L.

MCPA and clomazone concentrations are found to be always below 0.02 μg/L (Figure 8). Note that, in general, in the case of groundwater sampled below 1 m depth, according to Directive 2006/118/EC a concentration of 0.1 μg/L should be considered as the end-point, which means that concentrations above this threshold are to be considered high and posing a risk in terms of water quality (Voccia et al., 2024; Dolan et al., 2013). In this study, groundwater is sampled from small piezometers and therefore when sampling more than 1 L of water as in this case, it is difficult to refer it to a specific depth, since a significant portion of piezometer is emptied.

The statistical analysis did not show any significant difference among herbicide concentrations detected in the three piezometers.

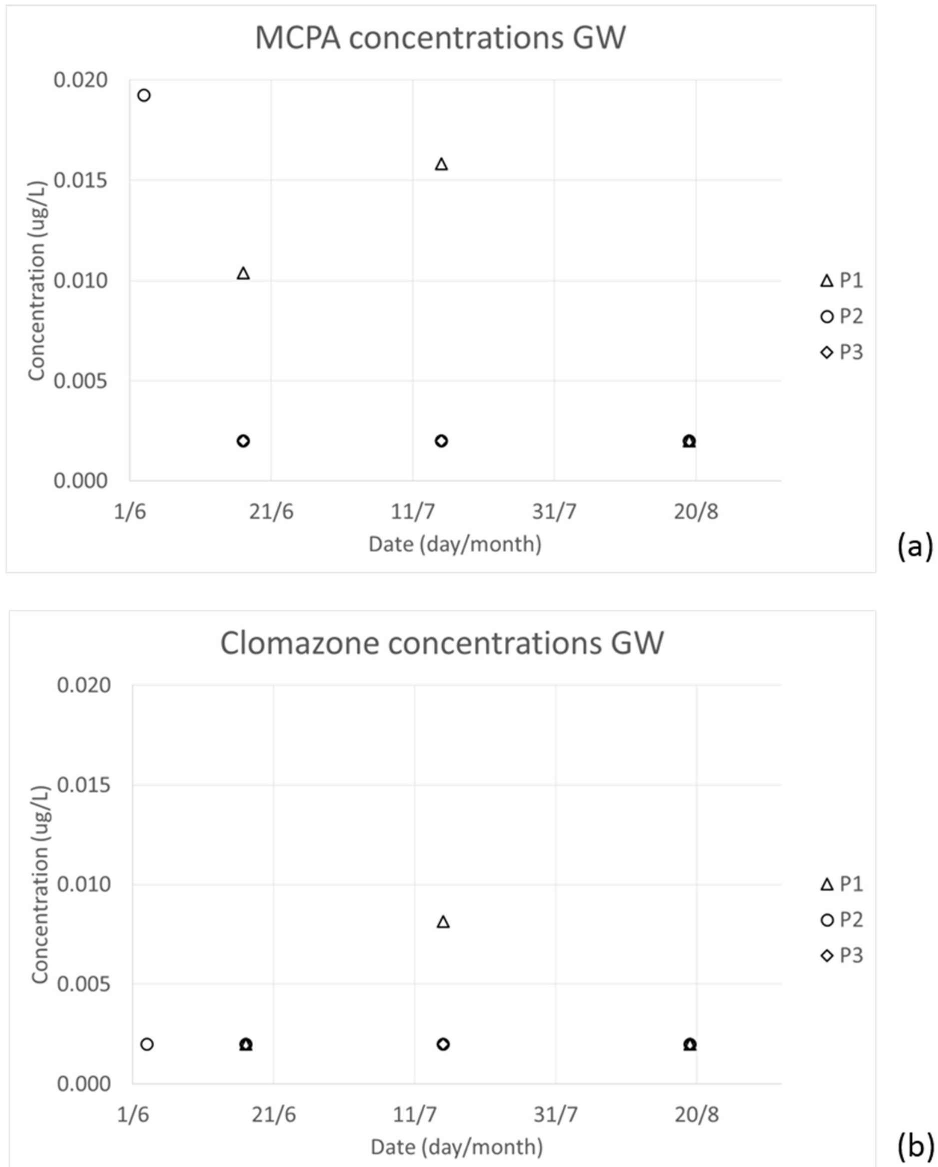


Fig. 8 MCPA (a) and clomazone (b) concentrations (µg/L) monitored in the piezometers sampled (P1, P2, and P3)

These results are consistent with the data monitored by ARPA in the neighbourhood of the district in the period 2019-2021, when data are available. For both MCPA and clomazone, concentrations found in 4 different sampling points (i.e., Valle Lomellina, Ferrera Erbognone, Tromello and Lomello) are always <0.03 µg/L, apart from a single case in which clomazone was detected at a concentration of 0.04 µg/L (Lomello, 27th May 2021). Nevertheless, it must be noted that ARPA samples groundwater in April-May and October-November and not during the agricultural season as it was done in the present study. In addition to that, the ARPA groundwater monitoring network includes both wells and piezometers with a length which is often >15 m, even if monitoring the phreatic aquifer. Nevertheless, three out of four ARPA groundwater monitoring points close to the San Giorgio district have a length <15 m and thus the concentrations detected are expected to be lower but more comparable with those acquired in the piezometers used in this study, which are shallower and intercept the upper part of the phreatic groundwater table during the irrigation season.

A 4-year study performed in Catalonia (Spain), which monitored 18 different groundwater bodies, reported MCPA maximum and average concentrations of 0.20 µg/L and 0.03 µg/L, respectively (Köck-Schulmeyer et al. 2014). These concentrations are approximately 10-fold higher than those presented in this study (maximum and average concentrations of 0.019 µg/L and 0.005 µg/L)

3.4. Nutrients in groundwater

As to nutrients in groundwater, we highlight that: (i) nitrogen, and nitrates in particular, may pose a problem for the area; and (ii) the three piezometers monitored show different results (average concentrations are higher in P3 than in P1 and P2, with statistically significant differences for total N and K between P1 and P3).

In the piezometers monitored, nutrients showed different behaviours (Figure 9). The maximum concentration of total N detected in the samples is 24.56 mg/L, the minimum is 0.28 mg/L and the mean value is 8.23 mg/L. In the case of $P\text{-}PO_4$, the maximum concentration is 2.02 mg/L, the minimum is 0.19 mg/L and the mean value is 0.68 mg/L. As to K, the maximum is 87.80 mg/L, the minimum is <LOQ and the mean value is 29.36 mg/L. For total N and K, losses resulted to be higher in P3 (average concentration of 20.08 mg/L for total N and 78.90 mg/L for K) than in P2 (4.22 mg/L and 6.06 mg/L for total N and K, respectively) than in P1 (0.38 mg/L of total N and <LOQ for K). In the case of $P\text{-}PO_4$, P3 still shows the highest concentrations (average of 0.89 mg/L), followed by P1 (0.84 mg/L), and P2 (0.32 mg/L). The statistical analysis performed shows significant differences only between P1 and P3 for both N and K levels, with higher N and K concentrations in P3 than in P1. No statistically significant differences are observed in P concentrations in the different piezometers. It should be noted that in P3 the legal limit for nitrates of 50 mg/L is always exceeded (detected values of nitrates are: 108 mg/L, 80.8 mg/L, 76.2 mg/L). Being downstream of the district, well P3 (Figure 1, Cascina Brelle) could indicate a high nitrate contribution to groundwater quality that occurred in the district. However, the high N concentrations found in P3 could be due to a generalized groundwater pollution, as values do not show a decreasing trend along the season and possibly other contributions than rice occur. In fact, human contribution to nutrient concentration in surface water and groundwater include many activities other than rice cropping (e.g., other crops, livestock, civil contribution) (Lerner, 2007; Bijay-

Singh and Craswell, 2021). By the way, sources of contamination near the well may be more important than those further upstream in determining the quality of the sampled water. Nutrients in groundwater might be also due to losses from civil sewage pipes (Wakida and Lerner, 2005; Nguyen and Venohr, 2021). In this sense, nutrient concentration in P2 could be higher compared to P1 due to the proximity to the urbanized area (town centre).

Another study performed in Lomellina (Gosetti et al., 2019) showed maximum concentrations of total N, P-PO_4 and K comparable with the present study. Gosetti et al. (2019) recorded the following maximum concentrations in 2015-2016: 22.4 mg/L of total N, 0.95 mg/L of P, and 91.3 mg/L of K. It should be noted that Gosetti et al. (2019) sampled the groundwater in piezometers similar to those used in the present study, but installed close to rice paddies, since the study was conducted at the farm scale in a rice farm.

By comparing data collected in the present study with the data monitored in the surrounding area by ARPA in 2021, it is possible to note that the latter values are much lower (total N ranging between <1 and 8.7 mg/L, total P between 0.17 and < 0.05 mg/L, K between 1.5 and 2.3 mg/L). However, ARPA monitoring skips the whole agricultural season (as samples were taken in May and October); as a consequence, data cannot be directly compared to the dataset collected in this study. As to nutrients in groundwater, limits imposed by the Italian legislation are the following (reported by the 'Gazzetta Ufficiale della Repubblica Italiana' – serie generale n.165): nitrates 50 mg/L, nitrites 0.5 mg/L, ammonium 0.5 mg/L. Instead, K and P have no limits, although the fixed residue values (of the sum of N, P, and K) cannot exceed 1500 mg/L. All samples resulted to be within this limit; however, among all the groundwater samples collected, 30% exceeded law limit for nitrates, but law limits for both ammonia and nitrites are never exceeded. So, concerning N, the main issue for groundwater in the district is related to nitrates. According to 91/676/CEE directive, 4 quality classes can be established for nitrate concentrations in groundwater: 0-24 mg/L, 25-39 mg/L, 40-50 mg/L, and >50 mg/L. Considering all samples, 60% of them fall in the first class, 10% in the second class, and 30% in the fourth and worst class. In particular, P1 nitrate concentrations are always in the first class, P2 in the first and second classes, and P3 always in the fourth class.

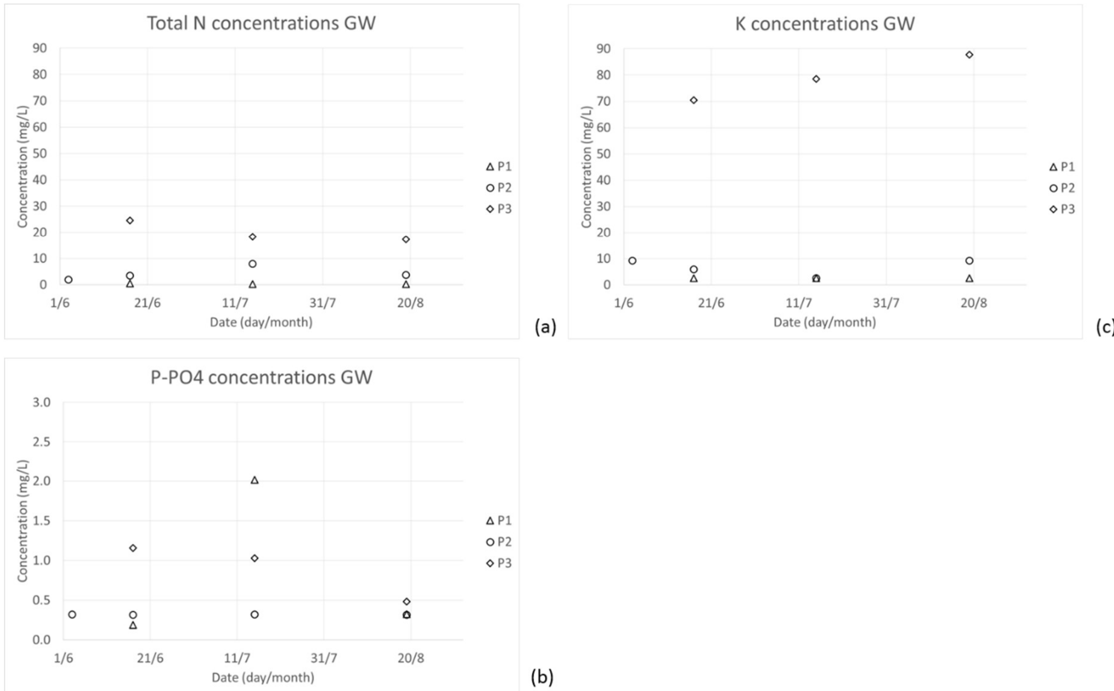


Fig. 9 Nutrient concentrations (mg/L) monitored in the piezometers sampled: total N (a), P-PO_4 (b), and K (c)

4. Conclusions

This study investigated the presence of two commonly used herbicides in rice cropping (i.e., MCPA and clomazone) and nutrients in surface water and groundwater of the San Giorgio di Lomellina irrigation district, located in the Lombardy-Piedmont rice area. Being sample collection and analysis very expensive and time-consuming activities, this study was limited in time - one single agricultural season, 2021 - and in space - San Giorgio di Lomellina district, extending for 1000 ha. Although a longer and more widespread monitoring activity would be needed to better assess surface water and groundwater quality in the whole Lombardy-Piedmont rice area, which is the most important in Europe, we consider the district to be well representative of the surrounding agricultural land, both in terms of land use and groundwater table depth. Thus, the findings of this study can give a first insight into the impact of rice farming in the Lombardy-Piedmont regions on water resources.

As to herbicides, data at the inlet and at the outlet of the district are comparable: MCPA average concentration is 1.13 µg/L (min <LOQ – max 5.7 µg/L, excluding the peak of 13.56 µg/L from the STP) at the inlet, and 0.48 µg/L (min <LOQ – max 5.98 µg/L) at the outlet. This means that surface water quality does not seem to degrade due to MCPA and clomazone treatments occurring in the district. As to groundwater, MCPA and clomazone concentrations monitored are always below 0.02 µg/L, showing a little impact on groundwater quality related to these two herbicides. Because of the

differences observed between surface waters and groundwater, we can infer that the main pathway for MCPA and clomazone transport occurs along the surface river network (e.g., runoff).

As far as nutrients are concerned, they do not show significant trends in surface waters along the season. This may be due to the fact that nutrient sources can be many and include sources other than rice (e.g., other crops, civil contribution, livestock). Total N average concentration is 2.10 mg/L (min 0.17 mg/L – max 7.82 mg/L) at the inlet and 2.33 mg/L (min 1.25 mg/L – max 3.57 mg/L) at the outlet. P-PO_4 average concentration is 0.34 mg/L (min 0.02 mg/L – max 3.88 mg/L) at the inlet and 0.24 mg/L (min <LOQ – max 0.66 mg/L) at the outlet. K average concentration is 3.58 mg/L (min >LOQ – max 9.90 mg/L) at the inlet and 5.30 mg/L (min >LOQ – max 57.60 mg/L) at the outlet. When looking at N-NO_3, the average concentration is 1.12 mg/L (min 0.25 mg/L - max 3.73 mg/L) at the inlet, and 1.71 mg/L (min 0.73 mg/L - max 3.32 mg/L) at the outlet. In the case of groundwater, total N average concentration is 8.23 mg/L (min 0.28 mg/L – max 24.56 mg/L). P-PO_4 average concentration is 0.68 mg/L (min 0.19 mg/L – max 2.02 mg/L). As to K, the average concentration is 29.36 mg/L (min <LOQ – max 87.80 mg/L). Focusing on nitrates only, in P3 the legal limit of 50 mg/L is always exceeded. So monitoring results point to the fact that nitrates may be more of a problem for the area than herbicides, and this seem especially true for groundwater. For nitrates, however, the sources of origin may be many and varied, and a further study would be needed to understand if rice cropping could be considered the primary source of contamination for the area.

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Declarations

Ethics approval

This is an observational study with no ethical approval required. The MEDWATERICE project, in the frame of which this study was carried out, had no ethical issues. The research did not involve any of the following: human embryos and human foetuses, human participants, human cells or tissues, personal data, animals, third countries, dual use, misuse, nor other ethical issue.

Consent to Participate

Not applicable (see ethics approval)

Consent to Publish

Not applicable (see ethics approval)

Author Contributions

Arianna Facchi, Federico Ferrari, Olfa Gharsallah and Alice Tediosi designed the study. Data collection was performed by Federico Ferrari, Tommaso Ferrari, Lucio Botteri, Riccardo Rossi and Nicola Ballerini. Sample analysis was performed by Diego Voccia and Lucrezia Lamastra. The first draft of the manuscript was written by Alice Tediosi with contribution of Olfa Gharsallah and Diego Voccia. Giulio Gilardi supported with the graphic design of images. Arianna Facchi, Giulio Gilardi and Olfa Gharsallah commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose

Data availability statement

The data supporting the results reported in this paper can be obtained contacting alice.tediosi@aeiforia.eu