Off-site movement of quinclorac from rice fields

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Highlights

- *Quinclorac persistence in paddy water is affected by its residues in entering waters.*
- *Entering waters often contain quinclorac residues.*
- *A water holding period of at least 10 days may limit the offsite movement of quinclorac residues from paddy fields.*

Abstract

The off-site movement of quinclorac from rice paddies was studied in a district and field study during the 2014 and 2015 growing seasons. Quinclorac residues were monitored on in-field surface waters, and out-field water entering and leaving an irrigation district. The behaviour of quinclorac residues in paddy water pointed out that the movement of herbicides from interconnected paddies is not negligible. This phenomenon was particularly evident in the days following the re-flooding of paddies after spraying. The water entering the uphill paddy fields have partially flushed quinclorac residues in the downhill paddy fields. Both the district and the field studies, showed the continuous presence of quinclorac residues in inlet waters. Even because of the continuous uploading of residues from inlet waters, traces of quinclorac in paddy water were detected up to 70 DAT. The presence of quinclorac in inlet water could be related to phenomena of drainage and drift during herbicide application in the paddies located upstream. The analysis carried out on waters leaving the district showed the presence of quinclorac residues in all the outlet floodgates, particularly from the end of May and late August. The results of this study suggest that appropriate management practices adopted at field scale may be required to lower the water contamination at irrigation district level. Considering that the highest losses of quinclorac occurred during the first 10-15 days after its application, to prevent these losses could be helpful avoiding water discharge from the treated fields for at least this period of time. In addition, a deep effort must be laid upon education and training of farmers on these environmental thematic throughout specific initiatives organized by public and private stakeholders.

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Introduction

Quinclorac is a substitute quinolinecarboxyilic acid which belongs to the class of auxin herbicides (Grossmann, 1998). Firstly introduced in Spain and Korea in 1989, it can be applied in pre- and post-emergence of rice, turf and other crops (BCPC, 2012). Quinclorac controls effectively *Echinochloa* spp. and other annual grasses such as *Digitaria* spp., *Setaria* spp., and *Brachiaria* spp., as well as certain broad-leaved weeds including *Aeschynomene* spp., *Sesbania* spp. and *Monochoria* spp. (Street and Mueller, 1993; BCPC, 2012). This herbicide is currently used in many countries of the world, such as United States, Argentina and Brazil, while it is no longer authorized in the European Union.

The protection of water resources from contamination due to pesticides use is one of the main objectives of the European policy. The most important legislative tool set up by European Union is the Water Framework Directive ('2000/60/CE', 2000; European Union, 2000) but over the last years other directives ('2008/105/CE', 2008; '2009/128/CE', 2009 - European Union, 2008, 2009a) have defined more strict criteria in order to reduce pesticide transfer from site of application to water resources. Herbicides and their metabolites were the PPPs mostly detected in surface waters, while fungicides were the substances mainly found in groundwater (Parisse *et al*., 2020). The intensive use of plant protection product (PPPs), and herbicides in particular, may present risk to the environment and this is enhanced when pesticides are applied in rice, due to the strict connection with the water compartment (Resgalla *et al*., 2007; Ueji and Inao, 2008). Among the xenobiotics that can be found in water, PPPs are often found with high frequency by environmental authorities at national and regional scale. The last available report made by the Italian National Institute for Environmental Protection and Research (Parisse *et al*., 2020) showed PPPs residues on 77,3% and 35,9% of the monitored points in surface waters and groundwaters, respectively (Parisse *et al*., 2020). The presence of PPPs in water resources is also reported by several studies conducted in many regions of the world (Konstantinou *et al*., 2006; Guzzella *et al*., 2006; Silva *et al*., 2006; Marchesan *et al*., 2007; Albuquerque *et al*., 2016; Parisse *et al*., 2020; Tauchnitz *et al*., 2020). Contamination of water resources by PPPs in rice areas is quite common. The monitoring campaigns carried out by regional authorities in the Italian rice district report the presence of many pesticides, such as oxadiazon, tricyclazole, bentazone, and quinclorac. Quinclorac has been a herbicide of great interest in Italian rice fields for its high efficacy on *Echinochloa* species, and in particular on *E. phyllopogon* (Grossmann, 1998). On the base of the last data published by the Italian Institute for Environmental Protection and Research Institute (Paris *et al.*, 2018), during 2016 quinclorac was still detected in 82 monitored points of surface waters, although only in 13 sites (1% of sampling points), the concentrations detected exceeded the environmental quality standard for pesticides stated in the Directive 2000/60/EC (0.1 µg L^{-1}). In order to reduce the risk of water contamination, in 2009, the Italian Ministry of Health introduced restriction of use in Piemonte region ('DM 9/3/2007', 2007; Regione Piemonte, 2007). Later, quinclorac was not included in the Annex I of Regulation (EC) No 1107/2009 ('1107/2009/CE', 2009 European Union, 2009b). In Italy its use was allowed until 2017 by derogation of art. 28 of the Regulation ('1107/2009/CE', 2009 European Union, 2009b) related to emergency situations in plant protection for a maximum period of 120 days. In 2017 on the territory of Piemonte Region, quinclorac use in rice cultivation was allowed from April 11 to July 30, with the obligation for farmers to keep the floodgates closed during the first week after the treatment (Regione Piemonte, 2017). Yet, for several years quinclorac has received temporarily emergency authorizations in some EU countries (*e.g*. Italy, Spain) against *Echinochloa* spp. populations become resistant to others herbicides on the market. This study, conducted in 2014 and 2015, was aimed at understanding the off-site movement of quinclorac from rice paddies at a district and field level. The persistence of a certain pesticide in the environment is strongly affected by its physical and chemical properties. Specific field conditions, such as field submersion, may significantly alter the fate of pesticides and their dissipation routes and times (Santos *et al.*, 2000). Hence, even the dissipation of quinclorac in paddy field may be affected by these conditions. Quinclorac residues were monitored on in-field surface waters, and out-field water entering and leaving an irrigation district. The results of this study may be of interest to policy makers and technical advisors to highlight the reasonableness of adopting appropriate in-field management practices in order to reduce the transfer of quinclorac to water bodies. This information will be applicable both in areas where quinclorac is currently authorized and in case of temporary uses due to emergency situations in plant protection.

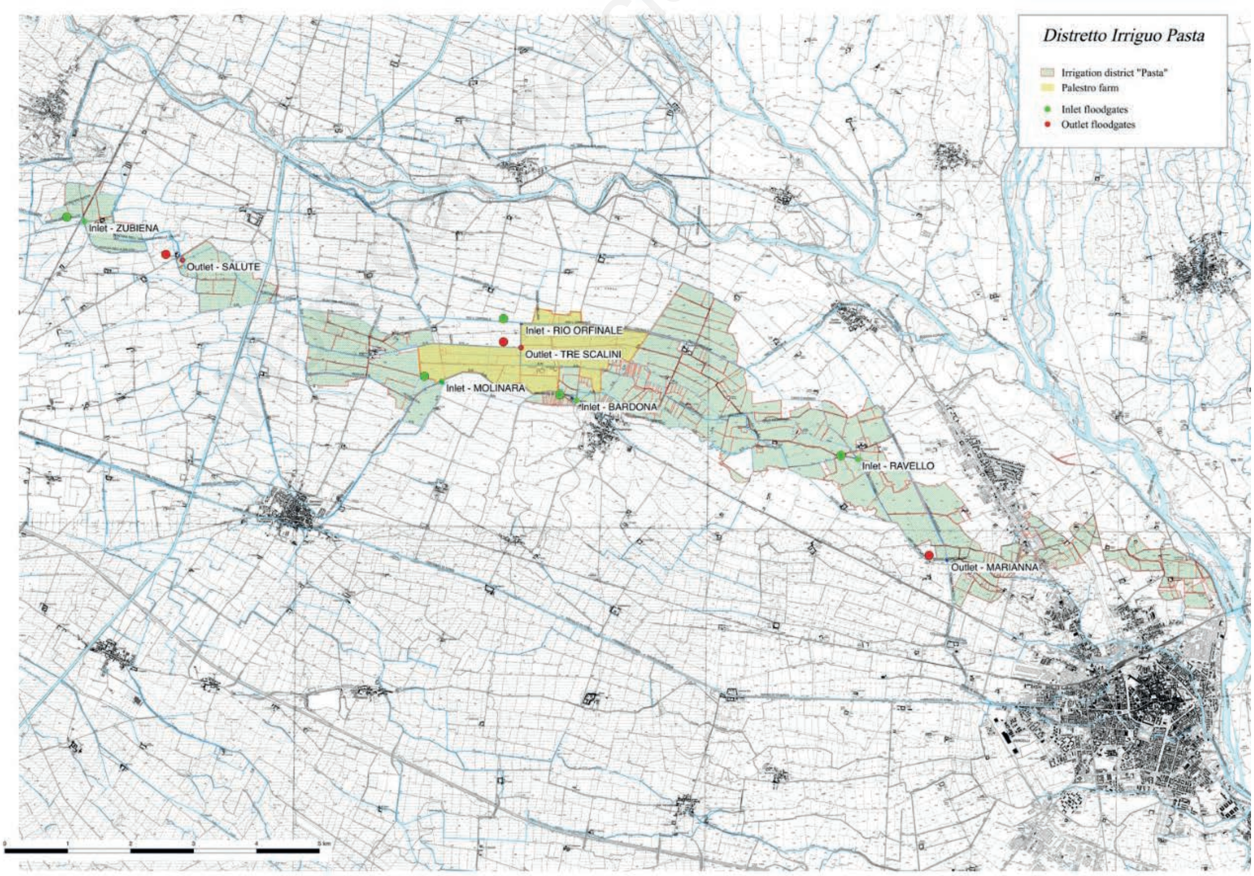

Figure 1. The 'Pasta' Irrigation District. On light-green the 'Tenuta Palestro' farm.

Materials and methods

Study area

The study has been carried out in the province of Vercelli, in the Piemonte Region, Northern Italy, one of the most important rice growing areas of Italy and Europe. The study has been conducted at district scale (*Distretto irriguo Pasta),* monitoring of quinclorac residues in surface water entering and leaving the irrigation district, and at *Field scale,* monitoring of quinclorac residues in 3 representative rice fields (Figure 1) of the '*Tenuta Palestro*' farm, located in the central part of the irrigation district. The district has a total area of more than 1400 ha and spans across the municipalities of San Germano Vercellese, Olcenengo, Quinto Vercellese, Caresanablot and Vercelli (Figure 1). The '*Tenuta Palestro*' is located in the central part of the 'Pasta' irrigation district under the municipality of Olcenengo (Vercelli); it has a size of about 233 ha, all cultivated with rice. The paddy fields monitored in the study were located in the western part of the farm and were represented by three interconnected adjacent fields. From the upmost to the bottommost, the three fields were named FIELD 1, FIELD 2 and FIELD 3, and had an area of 1.28, 2.09 and 2.04 ha, respectively (Figure 2).

The district scale monitoring, conducted during 2014 and 2015 growing seasons, was aimed at assessing the presence of quinclorac residues in surface water by considering watercourses that feed the irrigation district or drain water from it.

The field scale monitoring was finalized to better understand the behaviour of quinclorac within paddy fields managed according to the local common agricultural practices. The data collected from the district level should help to properly scale the findings obtained at field level.

Characteristics of the farms in the 'Pasta' district

A series of information regarding the main characteristics of the farms included in the irrigation district were collected by means of a questionnaire distributed to all farms present in the district. The survey was carried out in both years.

In 2014 a total of 30 out of 34 questionnaires initially distributed have been filled in. The farms that answered the questionnaire represented about 90% of the area of the district. In 2015, a total of 24 out of 34 questionnaires initially distributed have been filled in (that correspond about 70% of the area of the district). In both years the information collected might be considered well representative of the agricultural practices routinely applied in the district. The farms have an average size of 44 ha and they are cultivating rice mostly under flooded conditions; only few hectares are dry seeded. Clearfield® varieties represent about 30% of the cultivated varieties cultivated in the district. The majority of farms have the farmland totally included in the 'Pasta' irrigation district, while some others have only part of the fields falling in the district. In this second case the practices adopted in the fields within the irrigation district were considered as being the same of those routinely applied in the entire farm.

The questionnaire has also taken into account the use of quin-

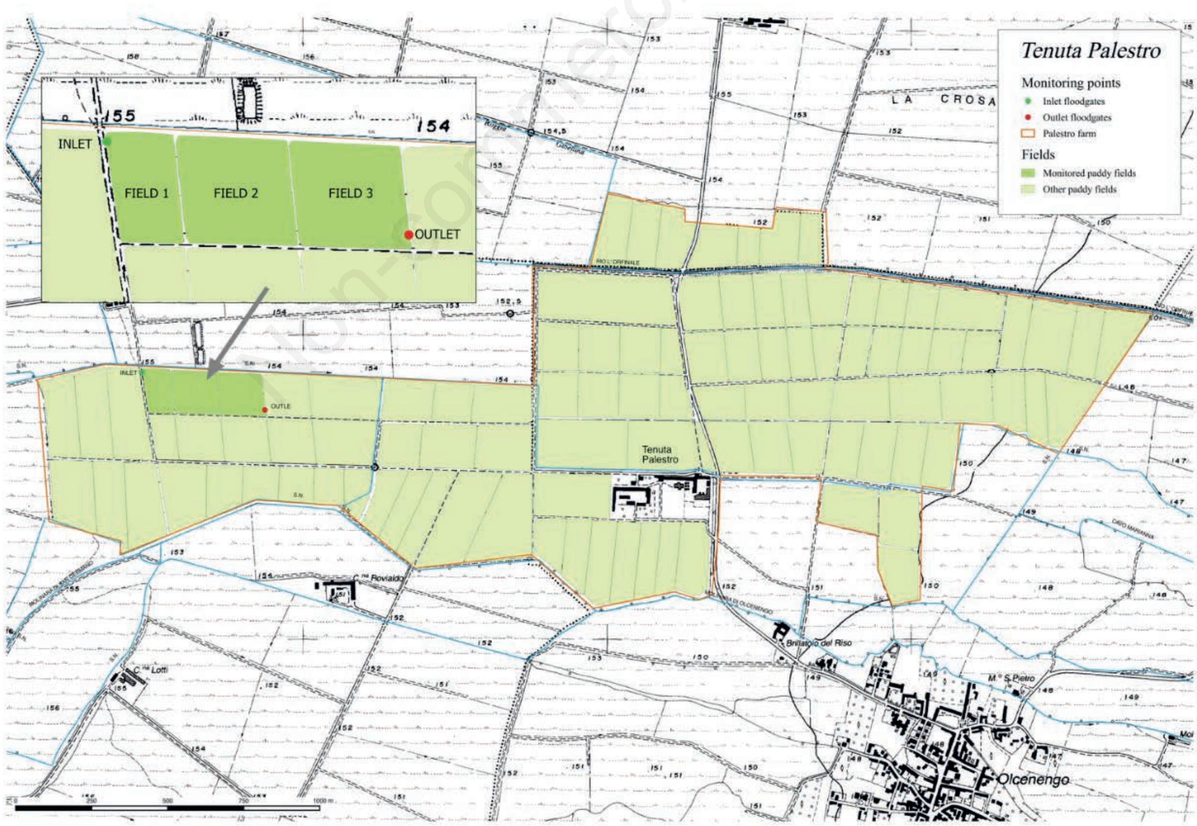

Figure 2. The '*Tenuta Palestro*' farm and the fields monitored in the field-level study.

clorac within the district. Quinclorac was routinely used by 67% of the farms in 2014 and by 71% the following year. In the two years, farmers declared that they applied quinclorac on about 60% of their paddy surface. The window of application for quinclorac resulted quite large; most of the farmers applied quinclorac between the end of May and first three decades of June (Figure 3).

Weed control strategies adopted in field-level study

The fields considered in the field-scale study were cultivated according to common local agronomic practices. The rice variety Ronaldo (Lugano seed company) was sown in the three fields on April 29th in 2014 and on April 30th in 2015 at a rate of 180 kg ha^{-1}. Fields were managed according the rice cultivation practices commonly adopted in the area, which consists of autumn-ploughing to incorporate rice residues, and broadcast seeding in spring on flooded fields. Main cropping practices, including herbicides treatments, are listed in Table 1. In 2014, a pre-seeding application of glyphosate (Roundup® 360 Power, Monsanto Agricoltura Italia) at a rate of 2.7 L ha^{-1} (972 g a.i. ha^{-1}) was done on March 7. On March 27, fields were treated with flufenacet (Cadou® Riso, Bayer CropScience Italia) at a rate of 0.7 kg ha^{-1} (420 g a.i. ha^{-1}), while on April 14, fields were sprayed with oxadiazon (Ronstar® FL, Bayer CropScience Italia) at a rate of 0.8 L/ha (304 g a.i. ha^{-1}). A treatment with the same herbicide was repeated at the time of sowing on April 29 at a rate of 0.12 L/ha (46 g a.i. ha^{-1}). Post-emergence weed control was carried out at two different moments. The first application was done on May 29 using a mixture of profoxydim (Aura®, Basf Italia) at a rate of 0.47 L/ha (94 g a.i. ha^{-1}), quinclorac (Facet® 250 SC, Basf Italia) at a rate 1.4 L/ha (350 g a.i. ha^{-1}) and MCPA (Fenoxilene®, Nufarm Italia) at a rate of 1.3 L/ha (289 g a.i. ha^{-1}). On June 20 a second post-emergence treatment was carried out with cyhalofop-butyl (ClincherTM One, Dow Agro Sciences Italia) at a rate of 0.43 L/ha (86 g a.i. ha^{-1}).

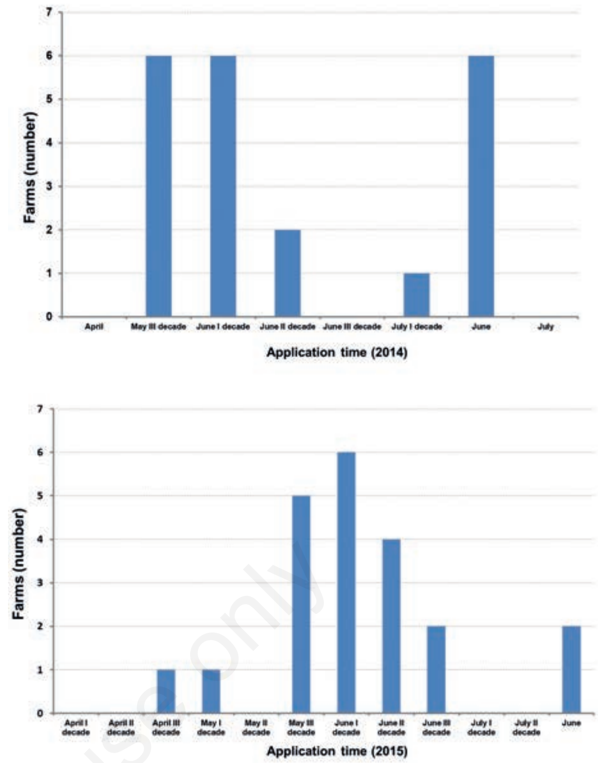

Figure 3. Period of application of quinclorac in 2014 and 2015 growing season. The bars represent the number of farms in which treatments were carried out in each application time. The bar called 'June' represent the farms where farmers answered indicating as a period of usage the entire month without specifying the decade.

Table 1. Main agronomic practices adopted in field-scale study in 2014 and 2015.

Date of execution 2014	Agronomic practice	Date of execution 2015	Agronomic practice
March 8-10/June 4-9/July 14	Fertilization	March 10-12/June 1/July 10	Fertilization
March 12-13	Harrowing	March 13-14	Harrowing
April 22	Flooding	March 25	Flooding
April 29	Sowing	April 30	Sowing
May 8 and May 28	Drying	May 9 and May 26	Drying
May 15 and June 1	Re-flooding	May 19-21-30	Re-flooding
August 20	Final drying	August 12	Final drying

Table 2. Monitoring points of the district.

Inlet floodgates Name	Coordinates	Outlet floodgates Name	Coordinates
Roggia Zubiena	45.39218° N; 8.20541° E	Tre scalini	45.37472° N; 8.29426° E
Rio Orfinale	45.37815° N; 8.29426° E	Roggia Marianna	45.34478° N; 8.38094° E
Roggia Molinara di Olcenengo	45.36979° N; 8.27822° E	Salute	45.38679° N; 8.22542° E
Roggia Bardona	45.36727° N; 8.30562° E		
Canale Ravello	45.35917° N; 8.36270° E		

During 2015, pre-seeding control of weeds was carried out at first on March 19 after a stale seed-bed technique with glyphosate (Roundup® 360 Power) at a rate of 2.7 L ha^{-1} (972 g a.i. ha^{-1}). Two different pre-seeding applications where done later using flufenacet (Cadou® WG, Bayer CropScience Italia) at a rate of 0.7 kg ha^{-1} (420 g a.i. ha^{-1}) on March 30, and with oxadiazon (Ronstar® FL) at a rate of 0.8 L/ha (304 g a.i. ha^{-1}) on April 15. Another application of oxadiazon (Ronstar® FL) was carried out on April 30 at a rate of 0.12 L/ha (46 g a.i. ha^{-1}). Post-emergence control of weeds was carried out on May 27 using a mixture of profoxydim (Aura®) at a rate of 0.5 L/ha (100 g a.i. ha^{-1}), quinclorac (Facet® 250 SC) at a rate 1.4 L ha^{-1} (350 g a.i. ha^{-1}) and MCPA (Fenoxilene®) at a rate of 1.4 L ha^{-1} (311 g a.i. ha^{-1}). A further post-emergence application was carried out June 19 with profoxydim (Aura®) at a rate of 0.85 L/ha (170 g a.i. ha^{-1}) and on June 23 with propanil (Stam® Novel Flo, UPL Italia), at a rate of 0.9 L/ha (432 g a.i. ha^{-1}). In both seasons, treatments were done by using a conventional tractor rear-mounted boom sprayer adjusted to deliver 350 L ha^{-1} of the herbicide mixtures.

District level study

Monitoring points

Both in 2014 and 2015, surface water samples were collected at 8 locations, 5 of which were at inlet floodgates, while the remaining 3 were discharge floodgates (Figure 1). The geographic localization of each monitoring points is reported on Table 2. The main characteristics of each sampling point are listed in the following paragraphs.

Inlet floodgates

1. *Roggia ZUBIENA* derives water from the *Canale De Pretis*, an artificial canal built in the half of nineteenth century to bring irrigation water from the river *Dora Baltea*. It runs across an intensively cultivated rice area. It is the main water supply of the district.
2. *Roggia BARDONA* derives water from *Roggia Molinara di Olcenengo*, which runs through the northern part of the municipality of Olcenengo and it finally converges in the *Roggia Marianna*.
3. *Canale RAVELLO* is the most downhill supply of the district and origins from *Rio Orfinale.*
4. *Roggia MOLINARA* derives water mainly from the canal *Naviglio di Ivrea*. It collects also drainages from paddy fields under the municipality of San Germano Vercellese.
5. *Rio ORFINALE* is fed by waters of *Roggia Gibellina* that runs west to east and collects also drainages from paddy fields.

Outlet floodgates

SALUTE floodgate is placed on the main discharge of the district. It collects also the excess waters from *Roggia Zubiena* in the case of abundant rains.

TRE SCALINI is placed in the neighbourhoods of 'Tenuta Palestro' farm.

Roggia MARIANNA is the most downhill outlet of the district and discharges water into *Roggione di Vercelli*, which is the main floodway of the district in the case of important rains.

Samples collection

In 2014 the monitoring of quinclorac in the irrigation district started in the second decade of May and continued up to the crop harvest. Samplings were conducted three times in May (all in the second and third decade), four times in June, three times in July, twice in August and September and once in October. In 2015 the monitoring of quinclorac started in the second decade of May and continued far after the harvest of the crop. Samplings were conducted two times in May (all in the third decade), four times in June, three times in July, twice in August and September and once in October. At each sampling date and for each sampling point, a bulk of 10 L of water was collected. Paddy water was gathered within each field by randomly filling a PTE 10 L tank. The overall number of samples collected was 30 in 2014 and 28 in 2015. From this bulk, a 1 L sample was then obtained. The samples were put into 1 L PTE flasks (Kartel, Noviglio, Italy) and immediately stored in a freezer room at −25°C until extraction and analysis.

Field level study

Monitoring points and sample collection

The monitoring points used in the field level study are indicated in Figure 2. Samples of paddy water were collected in 2014 at 5, 11, 12, 15, 21, 32, 36, 50 and 70 days after treatment with quinclorac (DAT). In 2015 samples were collected at 5, 7, 12, 15, 21, 30, 40, 50 and 70 DAT. At each sampling date a bulk of 10 L of water was collected. Paddy water was gathered within each field by randomly filling a polyethylene terephthalate (PTE) 10 L tank. From this bulk, a 1 L sample was then obtained. The samples were put into 1 L PTE flasks (Kartel, Noviglio, Italy) and immediately stored in a freezer room at –25°C until extraction and analysis. During 2014 a total of 50 samples was collected including paddy (30), inlet (10) and outlet (10) waters. In 2015, 27 samples of paddy waters and 9 samples each for inlet and outlet waters, were collected.

Analytical determination of quinclorac in water

Extraction from water samples

Quinclorac was extracted from the water by solid phase extraction (SPE). Before the extraction, the samples were previously filtered through filter paper (Cartiera di Cordenons, Italy) remove the impurities and the resulting filtered water was brought to pH 2 by adding 1 mL of H_3PO_4 0.1%. The extraction was performed by using single disposable cartridges (BakerBond C18, 6 mL, 0.2 g sorbent material). Each cartridge was conditioned with 12 mL of acetonitrile (Sigma Aldrich, Germany) and then washed with 12 mL of water brought to pH 2. The entire volume of the water sample (1 L) flowed through the cartridges under vacuum at a flow of 500 mL h^{-1}. The cartridges were washed with 12 mL of acidified water (pH 2). The adsorbed herbicide was eluted with acetonitrile until a final volume of 5 mL was reached. The eluted volume of 5 mL was then filtered through a 0.2 µm nylon filter (Wathman, USA) prior to LC-MS analysis.

LC/MS-MS analysis

The water extracts were analysed by LC-MS/MS using a Varian 310 triple quadrupole mass spectrometer, equipped with an electro spray ionization ESI source, a 212 LC pump, a ProStar 410 autosampler and dedicated software. LC separation was performed on a Phenomenex Luna® C18 R100 column, 5 µm, 50x2 mm. The mobile phase consisted of water (A) and acetonitrile (B) both containing 0.1% (V/V) acetic acid delivered at a flow rate of 0.2 mL min^{-1}. The gradient was from 90 to 10% in 10 min., then from 10 to 90% in 3 min, and finally maintained at 90% forward. The retention time was 6.5 min. Mass spectrometry analyses were performed in the positive ion mode, the nebulizing gas and the drying gas were N_2, both set at 25 psi; the drying gas temperature was 250°C, the capillary voltage was –30 V, and the collision gas was argon set at 1.8 mTorr.

Recovery and quantification limits

Quinclorac concentration was determined relative to peak of analytical standard solutions. Analytical-grade quinclorac supplied by Sigma Aldrich (Germany), was used as analytical standard. The mean recovery of quinclorac in water was 100%±SD. The limit of quantification (LOQ) achieved was 50 ng L^{-1}. The limit of detection (LOD) achieved was 5 ng L^{-1}.

Results

District scale study

In 2014, quinclorac residues were found in inlet waters during almost all the growing season at concentrations always below 5 µg L^{-1} (Table 3). Throughout the season the concentration peaks were observed in the second decade of June and in the first decade of July. The highest concentrations were measured on June 12 at Roggia Bardona (4.99 µg L^{-1}), and in June 19 at Canale Ravello (2.58 µg L^{-1}) and Roggia Molinara (1.27 µg L^{-1}). Another peak was measured on July 12 in water samples collected at Roggia Bardona (2.20 µg L^{-1}), Canale Ravello (1.49 µg L^{-1}), and Rio Orfinale (0.83 µg L^{-1}). Over the season, the lowest concentrations were always observed in water samples collected at Roggia Zubiena floodgate. The concentration peak that occurred on August 27 (Roggia Bardona, 0.47 µg L^{-1}) could be related with the beginning of the operations of discharging of paddy fields in the areas upstream. The maximum concentrations of quinclorac measured during the season at the outlet floodgates basically occurred at the same dates of the highest values observed at the inlet moni-

Table 3. Quinclorac concentration (µg L^{-1}) measured at the inlet monitoring points of the 'Pasta' irrigation district during the 2014 growing season (District scale study).

Sampling date	Concentration in INLET ditches (µg L^{-1})				
	Zubiena	Molinara	Orfinale	Bardona	Ravello
May 19	<0.05	<0.05	<0.05	<0.05	<0.05
May 28	<0.05	<0.05	<0.05	<0.05	0.24
May 31	<0.05	<0.05	<0.05	<0.05	0.05
June 6	<0.05	<0.05	0.24	0.05	0.15
June 12	<0.05	0.58	0.05	4.99	0.23
June 19	<0.05	1.27	0.27	0.86	2.58
June 26	0.05	0.49	0.12	1.03	0.27
July 4	<0.05	0.30	0.01	0.17	0.05
July 12	0.06	0.20	0.83	2.20	1.49
July 22	<0.05	<0.05	<0.05	0.08	0.00
August 12	<0.05	<0.05	<0.05	0.06	<0.05
August 27	<0.05	0.17	<0.05	0.47	<0.05
September 12	<0.05	<0.05	<0.05	<0.05	<0.05
September 24	<0.05	<0.05	<0.05	<0.05	<0.05
October 13	<0.05	<0.05	<0.05	<0.05	<0.05

Table 4. Quinclorac concentration (µg L^{-1}) measured at the outlet monitoring points of the 'Pasta' irrigation district during the 2014 growing season (District scale study).

Sampling date	Concentration in OUTLET ditches (µg L^{-1})		
	Tre scalini	Marianna	Salute
May 19	<0.05	<0.05	<0.05
May 28	0.40	<0.05	<0.05
May 31	<0.05	0.13	<0.05
June 6	0.10	0.20	<0.05
June 12	0.29	0.27	0.65
June 19	0.55	1.36	0.06
June 26	0.14	0.28	0.00
July 4	0.32	0.24	<0.05
July 12	<0.05	0.17	1.48
July 22	<0.05	0.17	<0.05
August 12	0.20	0.01	0.16
August 27	<0.05	0.03	<0.05
September 12	<0.05	0.14	<0.05
September 24	<0.05	<0.05	<0.05
October 13	0.40	<0.05	<0.05

toring points. The concentration peaks occurred, in fact, on June 12, June 19 (Roggia Marianna outlet, 1.36 μg L^{-1}), and at July 12 (Salute floodgate, 1.48 μg L^{-1}). The concentrations measured at the two most important discharges of the district, Salute and Roggia Marianna, never exceeded 1.5 μg L^{-1} (Table 4).

In 2015, during all the growing season quinclorac residues were frequently detected in most of the inlet floodgates (Tables 5 and 6). At the first sampling, carried out the day of quinclorac application in the Field scale monitoring study (May 27), residues of quinclorac were found only at the Rio Orfinale inlet floodgate (0.14 μg L^{-1}). At all the other floodgates, residues were below the limit of quantification.

However, already three days later (May 30), quinclorac residues were found in all the inlet floodgates, indicating that in the previous and/or current days quinclorac has been applied to the paddies located around the Pasta district. The maximum concentration was reached in Ravello floodgate on July 3 (3.78 μg L^{-1}). The inlet ditches Zubiena, Molinara, Rio Orfinale and Bardona showed an average season concentration of about 0.2 μg L^{-1}. At Ravello floodgate quinclorac residues were higher than those observed in the other inlet floodgates for all the season, with an average concentration of about 0.5 μg L^{-1}.

Residues of quinclorac were frequently found even in outlet floodgates. Two concentration peaks were recorded on May 30 at Tre Scalini floodgate (2.26 μg L^{-1}) and on June 25 at Roggia Marianna (5.79 μg L^{-1}). In the first case, the peak could be put in relation to the application of quinclorac carried out in the paddies of the Field scale study (on May 27). This floodgate is in fact close to the fields of the Palestro farm. The high concentration value observed on June 25, has likely to be put in relation to the fact that the Roggia Marianna outlet floodgate is the most downhill floodgate of the district, and collects waters from a relevant part of the

Table 5. Quinclorac concentration (μg L^{-1}) measured at the inlet monitoring points of the 'Pasta' irrigation district during the 2015 growing season (District scale study).

Sampling date	Concentration in INLET ditches (μg L^{-1})				
	Zubiena	Molinara	Orfinale	Bardona	Ravello
May 27	<0.05	<0.05	0.14	<0.05	<0.05
May 30	0.12	0.17	0.32	0.25	0.84
June 4	1.69	0.20	0.45	0.24	0.37
June 11	0.66	0.58	0.22	0.43	0.29
June 18	0.14	0.51	0.40	0.47	0.25
June 25	0.20	0.21	0.32	0.34	0.38
July 3	0.15	0.48	0.18	0.19	3.78
July 10	0.14	0.17	0.17	0.18	0.15
July 21	0.10	0.15	0.14	0.15	0.31
August 11	0.12	0.16	0.18	0.19	0.14
August 26	<0.05	0.15	<0.05	0.14	<0.05
September 11	<0.05	<0.05	<0.05	<0.05	<0.05
September 23	<0.05	<0.05	<0.05	<0.05	<0.05
October 15	<0.05	<0.05	<0.05	<0.05	<0.05

Table 6. Quinclorac concentration (μg L^{-1}) measured at the outlet monitoring points of the 'Pasta' irrigation district during the 2015 growing season (District scale study).

Sampling date	Concentration in OUTLET ditches (μg L^{-1})		
	Tre scalini	Marianna	Salute
May 27	<0.05	0.15	<0.05
May 30	2.26	0.30	0.11
June 4	0.36	0.27	0.40
June 11	1.01	0.39	0.16
June 18	0.67	0.88	0.16
June 25	0.22	5.79	0.35
July 3	0.16	0.53	0.22
July 10	0.23	0.20	0.14
July 21	0.14	0.17	<0.05
August 11	0.18	0.17	<0.05
August 26	<0.05	0.11	<0.05
September 11	<0.05	0.11	<0.05
September 23	<0.05	<0.05	<0.05
October 15	<0.05	<0.05	<0.05

district. Overall, the highest concentration values were detected between the second and the third decade of June. This is not surprising, considering that, as from the results of the questionnaire distributed to the farmers of the district, most of the quinclorac is applied in the same temporal window. At Salute floodgate, quinclorac residues were below the limit of quantification after July 10, while in the other two floodgates traces of quinclorac were found until August 27 (Tre Scalini) and September 11 (Roggia Marianna).

Field scale study - 2014

In Tables 7 and 8 are reported the concentrations of quinclorac found in paddy water, inlet and outlet waters during the 2014-2015 growing season. In 2014, quinclorac application was carried out at the end of May on drained fields. After the treatment, the fields were kept drained until 5 days after treatment (DAT), then they were submerged again; for this reason, during these days it was not possible to collect samples from the paddies. At the first sampling (5 DAT), quinclorac residues were found in all the fields with concentrations of 0.98 μg L^{-1}, 1.10 μg L^{-1}, 4.06 μg L^{-1}, in FIELD 1, FIELD 2 and FIELD 3, respectively. The gradient of increasing residue concentration from FIELD 1 to FIELD 3 was observed up to 12 DAT. At 15 DAT, the concentration of quinclorac in the three fields was not higher than 0.5 μg L^{-1}. A slight increase in quinclorac concentration (0.52 μg L^{-1}, as average of the three fields) was measured at 21 DAT, most likely because of the increase in quinclorac concentration recorded in inlet water at the same date. Quinclorac concentrations remained similar in FIELD 1 at 32 DAT. Afterwards, quinclorac residues were still detectable up to 70 DAT, even though at concentrations lower than 0.40 μg L^{-1}. In the inlet water, quinclorac concentration rose from 0.92 μg L^{-1}, before herbicide application in the monitored fields, up to 4.43 μg L^{-1} at 11 DAT. Afterwards, the concentration dropped to 0.40 μg L^{-1} at 15 DAT, increased again to 2.36 μg L^{-1} at 21 DAT, and then lowered to values never exceeding 0.40 μg L^{-1}. At 70 DAT, quinclorac concentration was below LOQ in FIELD 2. As expected, in outlet waters the highest concentrations of quinclorac were measured during the first two sampling dates (5 DAT and 11 DAT). Fifteen days after herbicides spraying, quinclorac residues in outlet waters did not exceed 0.25 μg L^{-1} and at 70 DAT they were close to the LOQ.

In 2015, quinclorac was sprayed to the fields on May 27. After herbicide application, fields were maintained drained for three days, then they were re-flooded. For this reason, until 5 DAT it was not possible to collect any water sample. At the first sampling (5 DAT) quinclorac was found in all fields under monitoring. The highest concentration was observed in FIELD 2 (6.48 μg L^{-1}), while in the other two fields concentration values ranged from 0.84 μg L^{-1} to 2.23 μg L^{-1}, in FIELD 1 and FIELD 3, respectively. The high concentration observed in FIELD 2 is likely due to the interconnection that exists between the three fields. In the first period of the submersion, water tends to move more or less rapidly from

Table 7. Quinclorac concentration (μg L^{-1}) measured in flooding paddy water and in the inlet and outlet floodgates water of monitored fields in 'Tenuta Palestro' farm during the 2014 growing season (Field scale study).

Days after treatment	Concentration in flooding water (μg L^{-1})			Concentration in Inlet and outlet water (μg L^{-1})	
	FIELD 1	FIELD 2	FIELD 3	INLET	OUTLET
–9	-	-	-	<0.05	<0.05
5	0.98	1.10	4.06	0.92	5.85
11	0.35	1.00	2.10	2.71	1.56
12	0.46	1.1	1.39	4.43	0.41
15	0.39	0.32	0.34	0.40	0.40
21	0.50	0.44	0.62	2.36	0.19
32	0.68	0.20	0.32	0.23	0.24
36	0.03	0.17	0.37	0.40	0.19
50	0.14	<0.05	0.25	0.1	0.1
70	0.13	<0.05	0.1	<0.05	<0.05

Table 8. Quinclorac concentration (μg L^{-1}) measured in flooding paddy water, and in the inlet and outlet floodgates water of monitored fields in 'Tenuta Palestro' farm during the 2015 growing season (Field scale study).

Days after treatment	Concentration in flooding water (μg L^{-1})			Concentration in Inlet and outlet water (μg L^{-1})	
	FIELD 1	FIELD 2	FIELD 3	INLET	OUTLET
5	0.84	6.48	2.23	0.57	7.91
7	1.42	0.54	11.65	0.40	-
12	0.26	0.41	1.34	3.22	0.78
15	0.57	0.31	2.66	0.48	0.96
21	0.64	0.22	0.35	0.53	0.80
30	0.16	0.33	6.31	1.78	0.43
40	0.16	0.56	0.24	0.59	0.26
50	0.13	0.12	0.38	0.29	0.24
70	0.11	0.14	1.55	0.08	0.36

the inlet floodgate of the FIELD 1 to the floodgate in communication with the following field (FIELD 2). This phenomenon was observed even at the following sampling (7 DAT) were the highest quinclorac residues were found in FIELD 3 (11.65 μg L^{-1}), indicating a gradual accumulation of quinclorac residues in the last field. With few exceptions, in FIELD 3 quinclorac residues remained, for most of the season, highest than those observed in FIELD 1 and FIELD 2. In particular, in FIELD 3, two concentration peaks were recorded at 7 DAT (11.65 μg L^{-1}) and 30 DAT (6.31 μg L^{-1}). The peak reached at 30 DAT could be also related to the high concentration of quinclorac observed in the inlet water (1.78 μg L^{-1}), the highest value recorded during all the season. In FIELD 1, starting from a month after the treatment, quinclorac residues in paddy water did not exceed 0.16 μg L^{-1}. In FIELD 2 a similar gradual decrease in quinclorac concentrations was observed, with the exception of the sampling at 40 DAT (0.56 μg L^{-1}).

Quinclorac residues were always found in inlet water. During the season, its concentration ranged from 0.08 μg L^{-1} (70 DAT) to 3.22 μg L^{-1} (12 DAT). The highest concentrations in inlet water were detected in the periods where quinclorac is usually applied to the fields. In particular at 12 DAT and at 30 DAT quinclorac residues in inlet water were 3.22 μg L^{-1} and 1.78 μg L^{-1}, respectively. In outlet waters, the maximum residue concentration (7.9 μg L^{-1}) was observed at the first sampling (5 DAT). At 7 DAT no water flowed out from the floodgate, thus any sample was collected. At the following samplings the concentration recorded in outlet waters gradually decreased, even though at 70 DAT a concentration of about 0.4 μg L^{-1} was still found.

Discussion and conclusions

The risk of water contamination by pesticides or their metabolites is generally more relevant in certain agroecosystems, as rice paddies, where fields are flooded (Ueji and Inao, 2008; Lamers *et al.*, 2011). The present study was aimed at pointing out the off-site movement of quinclorac in surface and paddy waters at a field and district level. Quinclorac is a herbicide largely applied across the world to control different weed species in rice and other agricultural crops; its presence in water resources is reported by several studies worldwide. In monitoring studies conducted from 1998 to 2000 in Brazil, residues of quinclorac were found in five of the seven hydrographic basins under survey (Resgalla *et al.*, 2007). Similar findings were reported by monitoring studies carried out in Italy since 2003 (Paris *et al.*, 2004).

The mobility of a certain pesticide in the environment is affected by several physical and chemical factors, related to soil properties, pesticide properties and crop management practices (Kerle *et al.*, 1994; Santos *et al.*, 2000). Two properties influence at most the movement of pesticides in soil and may consequently affect the magnitude of water contamination: the soil sorption coefficient and the soil half-life (Carter, 2000). In general, the longer the persistence of a chemical, the higher the risk of water contamination. About the soil properties, the content of organic matter, as well as the texture, may have an influence on quinclorac movement and dissipation. The higher the organic matter content and the amount of clay in the soil, the higher will be the sorption of quinclorac on the soil matrix and lesser the amount of the chemical leached (Hill *et al.*, 2000; Adams and Lym, 2015). The adsorption of quinclorac to organic matter is also favoured by its chemical nature, being the chemical an auxin herbicide (Kyung *et al.*, 1997). In a study conducted on a clay-loam soil quinclorac leached trough the soil after important simulated rainfall and the rate of quinclorac dissipation decreased with lower soil moisture (Hill *et al.*, 1998). The same authors reported that different moisture regimes affected quinclorac dissipation. Soil persistence of quinclorac may varies according the soil conditions. Dissipation in field is generally more rapid compared to that obtained from laboratory studies and varies from 7 days to a month, according soil conditions (APVMA, 2005; Miao *et al.*, 2014; Zhong *et al.*, 2018; Wang and Crosby, 1990). Even though we did not assess quinclorac dissipation in the soil because without of the scope of the study, the studied paddy fields were characterized by a sub-acidic soil reaction, with a low content of organic matter. Hence, a similar dissipation pattern may likely be assumed. The behaviour of the herbicide in water compartment can be affected both from the practices adopted after its distribution and from the presence of residues in entering waters. According to the label prescriptions, quinclorac must be applied on drained paddies, then fields must be gradually reflooded not early 5 days after herbicide spraying. The occurrence of flooding conditions after spraying may certainly facilitate the transfer of the herbicide from paddy fields to water bodies.

Overall, the fate of quinclorac in water environment has been less investigated. According to Williams *et al*. (2004), quinclorac tends to be water displaced, resulting also more vulnerable to leaching at higher pH values. Compared to other auxin herbicides, quinclorac showed a lower solubility in water (0.065 mg kg^{-1} at pH 7, 20°C) (BCPC, 2012) and it results not affected by hydrolysis at different pH values (5, 7 and 9) (Serafini, 2001; Pareja *et al.*, 2012). The low water solubility of quinclorac should reduce the risk of transfer of this chemical to waters. According to the regional soil classification map, fields used in the present study show a high protecting capacity towards ground water. However, the long persistence of quinclorac in soil extends the period during which the chemical can be transported away from the site of application by different phenomena. Pareja *et al*. (2012) founds that quinclorac is substantially stable to photolysis, while photocatalysis occurred faster in ultrapure water compared to paddy water due to its natural turbidity. The presence of dissolved organic matter may, in addition, affect pesticide photodegradation (Pinna and Pusino, 2012). The same authors found that photodegradation of quinclorac did not occur after irradiation by UV and simulated sunlight, unless in presence of a photocatalyst. According to a study carried out in Brazil by Zanella *et al*. (2011), quinclorac shows a half-life of about 10 days in paddy waters and residues of the herbicide were found up to 48 days after treatment. Other authors reported that quinclorac water half-life ranged from 21 days (dos Santos Miron *et al.*, 2005) to 31 days (Reimche *et al.*, 2008). Transfer of herbicides into water system is closely linked to several factors, such as paddy management practices, water management, physical-chemical properties of chemical applied, rainfall events (Ebise and Inoue, 2002; Ueji and Inao, 2008). According to the result of this study, quinclorac behaviour in field water was certainly affected by the continuous flow of residues with inlet waters. The interconnection between fields may indeed facilitate the development of a progressive accumulation of residues in the lowest fields, or in case of independent field, at the part close to the outlet floodgate. The results of this study allow to formulate some important considerations regarding the contamination of irrigation waters by quinclorac and its effect in terms of persistence of the herbicide in flooding water. In both years, even because of the continuous uploading of residues from inlet waters, traces of quinclorac in paddy water were detected up to 70 DAT. The transport of quinclorac from fields to water appears strictly related to the specific agricultural practices commonly adopted in rice cultivation.

The district study highlighted the presence of quinclorac residues in the water used to flood the fields. The presence of pesticide residues in the water entering the paddy fields has been reported by several studies (Ferrero *et al.*, 2001; Milan *et al.*, 2012). The concentration peaks observed in inlet water samples are in good keeping with the conventional period of application of quinclorac in the district, between the end of May and the first three decades of June. On the basis of the information collected with the questionnaire distributed to the farmers, more than 87% of quinclorac applications were carried out in June, 53% of them in the first decade of the month. An increased inputs of pesticides into waters from agricultural fields during the application season was also observed by Wittmer and Burkhardt (2009). The residues of quinclorac in inlet water might likely be due to drainage and/or spray drift during herbicide application in paddies located upstream the experimental site. This is in agreement with other studies conducted in paddy fields, which reported highest losses of herbicides in outlet waters shortly after their application (Milan *et al.*, 2019). Pesticide concentrations in channels and drainage canals increase generally after their application and they are related to the early release of water from the paddies (Phong *et al.*, 2010). The contamination is also attributable to drift during pesticide application. Overall, the monitoring conducted in inlet waters found quinclorac residues from the end of June until August, a period compatible with spraying times and the management practices carried out on paddy fields located out from the district. A similar behaviour was found by Resgalla *et al*. (2007) in a study conducted on several river basins in Brazil. The presence of pesticides in inflow irrigation and drainage waters was also assessed by Phong *et al*. (2010) in a paddy catchment in Japan.

The analysis carried out on waters leaving the district showed the presence of quinclorac residues in all the outlet floodgates, particularly from the end of May and late August. Within the district, farmers did not apply quinclorac at the same time; hence, the herbicides residues found in outlet waters reflect this variability in application timing. In both years, Roggia Marianna outlet floodgate showed the highest number of samples with concentration above the LOQ (0.05 μg L^{-1}). The high concentration peaks were also observed in this outlet floodgate, in the second and third decades of June. This was not totally unexpected, being Roggia Marianna the most downhill outlet of the district.

The behaviour of quinclorac residues in flooding water pointed out that the movement of herbicides from interconnected paddies is not negligible. This phenomenon was particularly evident in the days following the re-flooding of paddies after spraying. The water entering the uphill paddy fields have partially flushed quinclorac residues in the downhill paddy fields. The result is a gradual increase of quinclorac concentration detected in the flooding water of the downhill paddy fields. Similar results have been obtained for other herbicides in previous studies carried out in the same region (Milan *et al.*, 2012, 2019). In this study, quinclorac dissipation in flooding water was influenced by the level of contamination of the entering water (inlet water) that frequently contain residues of the herbicide and prolonged its persistence in paddy water. Peak concentrations were frequently found during the first 10-15 days after herbicide application; they were likely related to the spraying of quinclorac on other fields of the district. Farmer's interviews indicated that quinclorac is commonly applied from the end of May to the third decade of June, a period that overlaps with the period of the study. The results of this study suggest that appropriate management practices adopted at field scale may be required to lower the water contamination at irrigation district level. These may include measures for reducing contamination due to particle drift during spraying, such as the use of anti-drift nozzles, end-bar nozzles, a proper adjustment of boom height and spraying pressure, as well as the adoption of untreated respect areas along most vulnerable water streams (Marucco *et al.*, 2017). An adequate field levelling of the paddies, that ensures their regular and uniform submersion after spraying and a slow submersion of fields after spraying, may also limit the formation of concentration gradients within the paddies, as well as a slow release of water to paddies in the period just after pesticide spraying (Aravinna *et al.*, 2017). Another useful precaution could be the adoption of a water-holding period after the treatment, during which paddy water is stored in the paddy field. It has been highlighted that during this period, the initial concentration of many herbicides in paddy water may drop from 50 to 90% depending on the chemicals and thus limiting the runoff of paddy water from outlet floodgates can result in a strong reduction of the herbicide transfer far from the application site (Ferrero *et al.*, 2016). In Japan a water holding period of 3-4 days is recommended as a good agricultural practice to reduce pesticides transfer in water, even though an extension of water holding period to 10 days based on DT_{90} of herbicides has been suggested (Watanabe *et al.*, 2007). However, the results of the present study suggest that a water holding period of 10 days could not be sufficient to allow a significant reduction of quinclorac concentration in paddy water due to the input of residues with inlet water.

Another measure applicable in rice paddies to reduce the risk of herbicide transfer to water bodies could be the choice of other less mobile molecules. When planning the mitigation measures it should also be advisable to consider the risk of heavy rain events, which represent one of the most impacting weather extremes for Italian agriculture (Parisse *et al.*, 2020). Paddies must be properly managed in order to ensure the water storage within the fields during the water-holding period, even in case of heavy rain events. Climate change will modify the availability of water across country regions, either in terms of a reduction of the resource or the occurrence of extreme rain events (De Silva *et al.*, 2007).

The results of this study showed that quinclorac presence in paddy and surface water could be strongly affected by the agricultural practices adopted within fields. Considering that the highest losses of quinclorac occurred during the first 10-15 days after its application, to prevent these losses could be helpful avoiding water discharge from the treated fields for at least this period of time. However, this practice alone could not be sufficient to cause a significant reduction of the amount of quinclorac residues transferred from paddy fields to surface waters, but other best agricultural management practices should be adopted at a larger scale. In addition, a deep effort must be laid upon education and training of farmers on these environmental thematic throughout specific initiatives organized by public and private stakeholders. In the last years, many rice herbicides, despite not being included in Annex 1, were authorized for emergency use in order to control resistant weeds otherwise not controlled by current commercial products, as in the case of quinclorac. The management of resistant biotypes should not rely on active substances with emergency authorization but will require a joint effort between farmers - that should follow good agronomic practices to prevent resistance - and pesticide companies that should develop herbicides with new modes of action.

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