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2 **Monitoring of water quality inflow and outflow of a farm in Italian Padana plain for rice**
3 **cultivation: a case study of two years**
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45 **Abstract**

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47 Rice cultivation requires a large use of pesticides and nutrients to control weeds proliferation and
48 improve production. The water quality of four neighbouring rice fields located in the Lomellina
49 area (Italian Padana plain) was monitored in this study along the cultivation period (before, during
50 and after the period of planting), for two successive agricultural seasons (2015 and 2016). Two
51 paddy fields were traditionally cultivated with wet-seeding and the other ones with dry-seeding.
52 Eighteen sampling points were considered: 8 points for surface water, 2 points for underground
53 water, and 8 points for porous cups with 2 different depth. In order to evaluate the goodness of
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1 the paddy field system to maintain unchanged the quality of the inflow with respect to the
2 outflow water, three of the most used herbicides in Italian rice cultivation (imazamox, oxadiazon
3 and profoxydim) and other physical-chemical parameters were determined, namely biological
4 oxygen demand after 5 days, chemical oxygen demand, total suspended solids, anionic
5 surfactants, total hardness, total amount of phosphorus, nitrogen, and potassium and heavy metal
6 concentrations.
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11 In general, all the collected data confirmed that paddy fields did not contribute to worsen the
12 environmental pollution. The different flooding techniques adopted in the fields did not highlight
13 significant differences in concentrations of pesticides or metals. The pesticides reached their
14 maximum concentration (of the magnitude order of few ng mL^{-1}) in the day after the
15 administration and in the day after the application in the adjacent field. A slight reduction of total
16 As in grain was obtained adopting a dry period from the stem elongation up to booting. From the
17 collected data, it was possible to identify a general water flow direction in the paddy fields from
18 North-West to South-East: this prevailing flow direction was useful to understand not only the
19 diffusion of the pesticides and of their degradation products in the fields, but also that of the
20 nutrients.
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25 As concerns nutrients, it was important not to activate a recirculation of the water in the field during
26 the first 10 days from the administration, in order to avoid loss of nitrogen in the water vents or for
27 percolation. Moreover, the monitoring of potassium concentration allowed to avoid the use of
28 unnecessary potassic fertilization when there was already a high amount of this element in the
29 paddy field deriving from the irrigation.
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40 However, all the investigated water quality parameters were under the limits fixed by the European
41 Regulation. In addition, the presence of seven unexpected compounds was identified by non-target
42 approach in both campaigns in samples collected in the early summer period. Four of these
43 emerging contaminants were identified as N,N-diethyl-meta-toluamide, tricyclazole, amidosulfuron
44 and one of the imazamox photodegradation products.
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50 Although the low found concentrations of oxadiazon, tricyclazole and arsenic, in particular justified
51 a pre-existing contamination of the water inflow or of the investigated paddy area, the obtained
52 results supported the good quality of the paddy water outflow, confirming the rational use of the
53 water resource and the correct use of agronomic practices.
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60 **Keywords:** paddy water; water quality; non-target analysis; imazamox; oxadiazon; profoxydim
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Introduction

Rice is considered a high-value crop since it represents the most important ingredient in the diet of over half of the world population. However, rice production is affected by weeds proliferation that may sensibly reduce rice yields. To protect their crops, farmers widely employ combinations of herbicides, since they provide a pre-and post-emergence activity, due to the inhibition of plant enzymes production. In order to improve the production yields, nutrients are used, (based on nitrogen, phosphorus and potassium as macro elements). The worldwide consumption of herbicides represents 47.5% of the 2 million tons of pesticides consumed each year (Sopeña and Morillo 2009). Industries efforts are addressed to the design of new formulations characterized by high efficiency at low doses and low persistence in fields, in favour of the minimum environmental impact. However, the intrinsic features of these chemical (i.e. molecular weight, polarity, solubility and partition coefficient octanol/water) make pesticides able to spread in water, to leach into the soil or to evaporate, making their environmental impact evaluation of utmost importance.

Furthermore, since flooded shallow environments characterize rice cultivation, herbicides come in contact with paddy scenery through the draining of water into channels and, thanks to their mobility, they can contaminate areas not directly subjected to the phytosanitary treatments. Water resources contamination, in fact, is one of the major problems to deal with in order to ensure the conservation and sustainability of rice environment.

Recent studies pointed out that the problem is more complex than thought, in fact also the class of “emerging contaminants” which are able to alter environmental ecosystems must be considered. In particular, there is a growing interest in contaminants transformation products, since they could be more toxic and/or persistent than their precursors (Gosetti et al. 2010a, 2010b, 2015, 2018).

Literature studies deal with the monitoring of nutrients or selected pesticides in paddy fields and their spread in the surrounding environment (Gosetti et al. 2015, 2018, Moore et al. 2018), but often the transformation products of the investigated pesticides are not considered. Some studies concern the environmental loading in areas where rice paddies are predominant (Kawara et al. 1996, Zhou et al. 2003) or the reclaimed wastewater for the irrigation in paddy fields (Jang et al. 2008, Jang et al. 2010b, Jang et al. 2012, Kang et al. 2007), whereas other studies report the use of rice paddy mesocosms as filter systems for remediation purposes (Kang et al. 2006, Moore et al. 2018).

1 At last, other studies dealing with corrected and optimized practices of water management in
2 paddy fields (fertilizer applications, water reuse, limited and controlled use of allowed pesticides)
3 involve a reduction of water quality problems (Matsuno et al. 2006, Song et al. 2017) to improve
4 the rice production (Saptomo et al. 2015). It is frequent the use of model systems for predicting
5 pollutant loads, evaluating management practices, simulating hydrologic balance, or pesticide fate
6 within rice paddies (Choi et al. 2017, Inao et al, 2008, La et al. 2014, Li et al. 2018, Luo et al. 2012,
7 Seong et al. 2010, Song et al. 2016).

8 This study regards the water monitoring of a farm in an all-encompassing way and it focuses on
9 both the improvement of the fertilization and the correct administration of pesticides in order to
10 avoid excessive use of them that contribute polluting the environment. The monitoring campaign
11 occurred in 2015 and 2016.

12 The main objectives that we aim to achieve by the water monitoring are: i) reduce the nutrient
13 loading, if unnecessary; ii) minimize the As and Cd concentrations in rice by optimizing the water
14 management; iii) evaluate possible differences about dry-seeding and wet-seeding; iv) evaluate
15 the degradation time of pesticides and their permanence after the administration in paddy fields;
16 v) identify the transformation products of pesticides in paddy fields; vi) reduce as more as possible
17 the spread of pesticides after their administration in the fields. For this purpose, several water
18 quality parameters, metal's content, pesticides including their transformation products were taken
19 into account.

20 The evaluation of the water quality concerned a farm located in Padania plain (North Italy), in
21 which four rice fields were investigated. Two paddy fields were traditionally cultivated with wet-
22 seeding and other two fields were cultivated with dry-seeding, in order to evaluate if different
23 cultivation techniques can differently affect the water quality and therefore the potential different
24 impact of the present pollutants. Both surface water and groundwater of the considered paddy
25 area fields were investigated during two subsequent agricultural seasons (2015 and 2016) through
26 the identification of three of the most used herbicides in Italian rice crops, and of other possible
27 emerging contaminants. In fact, particular attention was also devoted to the identification of
28 unexpected compounds that might contribute polluting water, performing a non-target analytical
29 screening approach to search for the unknown compounds.

30 The herbicides monitored are imazamox (Ima, commercialized as Beyond™ containing 3.7% w/w
31 of the active principle Ima; 0.04 kg of Beyond™ for 200-300 L/ha), oxadiazon (Oxa, commercialized
32 as Ronstar™ containing 34.86% w/w of the active principle Oxa; 0.38 kg of Ronstar™ for 500

1 L/ha), and profoxydim (Pro, commercialized as AuraTM containing 20.6% w/w of the active
2 principle Pro; 0.20 kg of AuraTM for 200-300 L/ha) that act on acetolactate synthase,
3 protoporphyrinogen oxidase and acetyl CoA carboxylase of weed plants, respectively.
4 Moreover, the investigation of water quality parameters was carried out through the
5 determination of total hardness, biological oxygen demand (BOD₅), chemical oxygen demand
6 (COD), anionic surfactants, total suspended solids, amount of phosphorus, nitrogen and
7 potassium, and heavy metals among which cadmium (Cd) and arsenic (As) are particularly relevant
8 as they are both carcinogenic.
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10 These two toxic species are of utmost priority since the Codex Alimentarius (Codex Alimentarius
11 Commission, Thirty-seventh Session, 2014; Codex Alimentarius Commission, Twenty-ninth Session,
12 2006) limits their permitted concentrations in polished rice at 0.4 mg kg⁻¹ for Cd and 0.2 mg kg⁻¹
13 for As, considering their carcinogenicity. A detailed description of the selected water quality
14 parameters was reported in Online Resource 1.

15 All the collected data were used to monitor the selected parameters, trying to offer a
16 comprehensive study of the paddy field ecosystem, ensuring the safety of the water used to flood
17 the fields.
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19 **Materials and methods**

20 *Water samples*

21 Water samples were collected from an irrigation district representative of the Ticino-Sesia paddy
22 landscape in Northern Italy (Fig. 1). Four different fields were considered: fields 1 and 2 were
23 cultivated with dry-seeding and delayed flooding technique, while fields 3 and 4 with the wet-
24 seeding and continuous flooding one.

25 In order to investigate the contaminants, present in the water of the selected area, 18 sampling
26 points were considered: 8 points for surface water (labeled as "S" from "S1" to "S8", i.e. the
27 inflows and the outflows of the fields), 2 for underground water samples collected through
28 piezometers (*P1* placed upstream out of the farm and *P2* placed downstream in the farm between
29 fields 3 and 4) and 8 for the porous cups (the 4 cups labeled as "Ca" refer to 25 cm soil depth and
30 the 4 cups labeled as "Cb" refer to the 60 cm ones). All water samples were collected every two
31 weeks during the two agricultural seasons. The first agricultural season was since April the 15th to
32 September the 30th in 2015, for a total of 168 days, whereas the second agricultural season was
33 since April the 15th to October the 17^h in 2016, for a total of 185 days. The sampling frequency was
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daily and once a day for the week successive to the phytosanitary field's treatments, during the period in which fields were weeded.

The samples were collected, filtered on 0.2 μm PTFE filter (VWR International, Darmstadt, Germany) and immediately subjected to the analytical determinations. LC-MS/MS analyses were performed on all the samples collected (509 samples in 2015 and 558 samples in 2016), in order to monitor the concentrations of the three herbicides.

Reagents and apparatus

Oxadiazon (Oxa), imazamox (Ima), and profoxydim lithium salt (Pro) (analytical standard grade), water (LC-MS grade), methanol (LC-MS Ultra CHROMASOLV, >99.9%), ammonium acetate (eluent additive for LC-MS, $\geq 99.0\%$) and nitric acid ($\geq 69\%$) were purchased from Sigma-Aldrich (Milwaukee, Wisconsin, USA), while formic acid (98%) was purchased from Fluka (Buchs, Switzerland). Element stock solutions (Inorganic Ventures, Lakewood, USA) were used to perform external calibration in ICP-MS.

The three herbicides stock solutions were prepared in methanol at $50.0 \mu\text{g mL}^{-1}$ and preserved at 4°C in dark glass vials.

The LC-MS/MS analyses of the herbicides were performed using a micro LC system (Eksigent Technologies, Dublin, USA) that included a micro LC200 pump with a flow module of 5-50 μL and a CTC programmable array logic autosampler with a Peltier unit ($1-45^\circ\text{C}$). The system was coupled to a TripleTOFTM 5600+ system (Sciex, Concord, Canada) equipped with a DuoSprayTM ion source and calibrant delivery system (CDS). PeakViewTM 2.1 (Sciex, Concord, Canada) was adopted to investigate accurate mass spectral data, while MasterViewTM 1.1 (Sciex, Concord, Canada) was used to compare the intensities of mass spectral data among different samples. MultiQuantTM 3.0 (Sciex, Concord, Canada) was used to process and to quantify the herbicides in water samples. For the determination of metals an inductively coupled plasma with mass spectrometry (ICP-MS) 7700 Agilent Technologies (Agilent, Milano, Italy) equipped with a 3rd generation He reaction/collision cell and an autosampler ASX-500 Series G3286A (Agilent, Milano, Italy) was used. Detailed LC-MS/MS and ICP-MS instrumental conditions are reported in Online Resource 2. A CoFoMeGra solar box 3000e (Milan, Italy) equipped with a xenon lamp was used to simulate sunlight irradiation. A soda-lime glass UV-filter was used to better simulate outdoor exposure.

Photodegradation experiments

1 Photodegradation kinetics of the three herbicides in the paddy water was studied in order to
2 estimate the possible formation of degradation products.

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4 The solutions were prepared in paddy water (pH=8.7). In particular, Pro solution was prepared at
5 its maximum solubility in water at 26.5 mg L⁻¹ as reported by the EPA agency (US EPA, 2018a), and
6 the Ima solution was prepared at 30.0 mg L⁻¹. Oxa maximum water solubility was evaluated in our
7 laboratory since literature data reports different values (Garrigo et al. 2001; US EPA 2018b). A
8 calibration plot was built with standard solutions of Oxa dissolved in methanol, considering the
9 concentration range between 0.025 mg L⁻¹ and 5.0 mg L⁻¹; the obtained experimental water
10 solubility value was 0.10 mg L⁻¹.

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12 Quartz cells (volume of 14 mL) were filled with the pesticide solution, and subjected to solar box
13 irradiation at the proper sunlight conditions (irradiation intensity of the xenon lamp and
14 temperature were set at 800 W m⁻² and 35 °C, respectively) for 5 days, time sufficient for the
15 complete degradation, since after 5 days the pesticide concentration was no more quantifiable.
16 Aliquots of the solutions exposed to solar box irradiation were collected at the prefixed time,
17 filtered on a 0.2 µm PTFE filter (VWR International, Darmstadt, Germany), and then analyzed by
18 microLC-MS/MS in order to evaluate the degradation of the pesticide and the formation of
19 unknown photoproducts.
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35 *Analytical parameters for water quality*

36 To monitor surface quality water, biological oxygen demand (BOD₅) (Italian IRSA-CNR 5120
37 method 2003), chemical oxygen demand (COD) (Italian IRSA-CNR 5130 method 2003), total
38 suspended solids (Italian IRSA-CNR 2090 method 2003), anionic surfactants (Italian IRSA-CNR 5170
39 method 2003), total hardness (Italian IRSA-CNR 2040 method 2003), and total nitrogen (Italian
40 IRSA-CNR 4060 method 2003) were determined according to the IRSA APAT methods.

41 In order to evaluate possible variations of water quality during 2015 and 2016 agronomic
42 treatments, BOD₅, COD, total suspended solids, anionic surfactants, and total hardness were
43 determined only in samples collected from surface water, while total nitrogen was determined
44 both in surface and groundwater samples. The reason for this choice is mainly due to the fact of
45 obtaining immediate feedback on the status of surface paddy water that very heavily can influence
46 rice crop production. Moreover, the knowledge of the total nitrogen concentration in
47 groundwater permits efficient fertilization management in rice fields, since it depends on the soil
48 permeability and on the duration of the treatments in the fields.
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Results and discussion

Water quality parameters

The year average concentrations of the total nitrogen were not statistically different between the two monitored years (table 1a and table 2a). In particular, a decreasing trend was found for the samples collected from the porous cups within the same campaign. The total nitrogen concentrations in the *S* and *P* samples were almost constant also within the same campaign year. Table 2c reports the concentration values of the total hardness, the COD, and the anionic surfactants in the investigated surface water. The minimum, the maximum and the average concentration values of each parameter are reported for each sampling point.

As concerns the total hardness, the concentration range found (table 2c) could be attributed to the flood periods, in which water from different sources was used. The inflow water to the farm comes from the irrigation ditch Raina that originates from Lomellina North West and then continues to South East towards Agogna creek. Therefore, this irrigation ditch collects during its way the waste water of rice crops placed upstream. However, the average composition of the inflow water is relatively constant between one year and another (ISPRA 2018). The COD values are reported in table 2c and were always below the threshold limit of 160 mg L⁻¹ for the outflow into surface water (Italian Legislative Decree 152/06 2006) in 2015. Moreover, COD exhibited greater variability than BOD₅ (table 2b) and, in particular, it was about five times larger than BOD₅. COD and BOD₅ data indicate a low amount of organic material in water, highlighting a good and comparable quality of the water both in the inflows and in the outflows of the paddy fields. Since no significant variation of total hardness, COD and anionic surfactants was highlighted during 2015, in the second year of the campaign these parameters were not more monitored.

The anionic surfactants were never detected (all results below the LOQ = 0.05 mg L⁻¹, table 2c) for all the samples investigated in 2015, probably for the lack of water pollution contributions due to houses or industrial plants close to the paddy fields. For this reason, we chose to exclude this parameter from the water quality monitoring in 2016.

Table 1 reports the concentration values of N, P, K, As and Cd in the underground water and in the porous cups. The minimum, the maximum and the year average concentration values of each parameter were reported for each sampling point. Each average value of the year 2015 was

$$t_{calc} = \frac{(\bar{x}_1 - \bar{x}_2)}{S_{pooled} \sqrt{\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$$

1 compared though a t -test with the respective average value of the year 2016, in order to highlight
2 if significant differences of the considered parameter during the two years occurred. Therefore,
3 the table 1 reports the t_{calc} value calculated as follows:

4 where \bar{x}_1 and \bar{x}_2 are the average value of 2015 and 2016 years, respectively, n_1 and n_2 are the
5 number of months of campaign in 2015 and 2016, respectively ($n_1=6$ and $n_2=7$), and s_{pooled} is the
6 pooled standard deviation. Therefore, t_{calc} was compared with t_{tab} at 95% of confidence level and
7 with (n_1+n_2-2) degrees of freedom ($t_{tab(0.05;11)}=0.180$). Significant values of t_{calc} are reported in bold
8 in table 1. Similarly, table 2 reports the concentration values of N, P, K, As, Cd, BOD₅ and total
9 suspended solid (TSSs) in the surface water and the significance of the year average values.

10 The TSS average values (table 2b) were enough comparable between the two years and no
11 significant difference has been highlighted. In terms of TSSs, the best paddy water quality was at
12 the beginning of the campaign, in which the agronomic practices are poor or less intense than in
13 the following months with the only difference of the first month of the 2016 campaign, when
14 higher TSSs values ranging from 50 to 100 mg L⁻¹ were found in S7 and S8 (outflows of field 4) than
15 those found in S1 (inflow of the farm). A possible explanation could be the agricultural activity
16 made in the fields (e.g. seedbed preparation) during the month of April in 2016, in which heavy
17 rainfalls occurred. However, TSSs data confirm that paddy fields overall did not contribute to
18 worsen the environmental pollution.

36 ICP-MS determination

37 Standard calibration solutions were built at 12 concentration levels (LOQ, $5.0 \cdot 10^{-3}$, $1.0 \cdot 10^{-2}$,
38 $5.0 \cdot 10^{-2}$, $1.0 \cdot 10^{-1}$, 1.0, 5.0, 10, 20, 50, $1.0 \cdot 10^2$ and $2.0 \cdot 10^2$ ng mL⁻¹) replicating each level three
39 times. For each calibration curve, an F -test was performed to assess whether the models
40 explained a significant fraction of the information present in the measured data. All the F_{calc} were
41 greater than $F_{tab(0.01;1;34)} = 7.44$, therefore the plots explained a significant fraction of the
42 variance present in the data. The regression coefficients obtained were greater than 0.9990 and
43 the LOD and LOQ values are reported in Table 3.

44 As concerns the nutrient elements, P and K concentrations were determined in the porous cups,
45 as an estimation of the concentrations in the part of the soil for useful the plant. Phosphorus
46 concentration values (Table 1a) exhibited a similar trend in both campaigns: higher concentrations
47 (in the range of 600-700 ng mL⁻¹) were found in the samples collected from the porous cups at the
48 beginning of the campaign; then the P concentration values decreased up to a minimum of about
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100 ng mL⁻¹ at the end of the campaign. In addition, in 2015, P concentrations of *Ca* samples were greater of 6-28% than that of the *Cb* ones. As reported in the Table 1a, no significant difference has been noted between the two years of the campaign. As concerns surface water (Table 2a), significant differences can be found in *S4*, *S6* (outflow of field 1 and 3, respectively), whose concentration values are significantly lower in 2016. Moreover, a greater significant value of P concentration in *S8* (outflow of field 4) has been reported in the same year.

Furthermore, potassium, considered as one of the parameters useful to evaluate the nutrient conditions of paddy water, was found at greater concentrations in the samples collected from porous cups at 25 cm depth than in those collected from the corresponding porous cups at 60 cm depth. No significant trend was shown by the data collected from the porous cups and table 1a does not report any significant difference between the first and the second year. On the contrary, K concentration in the surface water is significantly different and in particular greater in 2016 than that determined in 2015 in *S2*, *S3*, *S5*, *S7* and *S8* (table 2a). A possible explanation is the greater starting K concentration (at the beginning of the 2016 campaign), which in turn can be retained from soil and successively released or spread towards the groundwater by percolation.

If the K balance (difference between the outflow concentration and inflow one) of the paddy fields before and after treatments was comparable, i.e. the contribution of agronomic practices did not affect or increase K concentration, a diverse situation was observed in the case of P. The highlighted different concentrations of P (the highest value in *S2* with respect to *S1*) can be explained considering a correct use of this nutrient within the paddy field.

Particular attention was devoted to the heavy metals: no significant concentration showing a high environmental impact was found in both the considered campaigns, except for As and Cd. Their presence in soil and irrigation water has to be considered a relevant factor affecting the accumulation of these species in the grain (Li et al. 2009). The specific timing of the aerobic and flooding conditions during different crop stages could be optimized in order to manage both Cd and As concentration in grain. The literature reports that water management in paddy fields influences Cd since flooding decreases Cd concentrations (Honma et al. 2016). Paddy field submersion decreases Cd concentrations in grains since such practice favours the formation of low soluble Cd sulfide and/or Cd carbonate in reducing soil conditions. Conversely, the same agricultural practice reduces As from arsenate (V) to arsenite (III) in solid soils, leading to greater availability of the metal in solutions, given the lower adsorption of As (III) than As (V).

1 Our data show a similar trend to those present in the literature since Cd concentration during the
2 period in which fields are submerged for more than three weeks is lower than that in the dry
3 period (Table 2b) (Arao et al. 2009; LaHue et al. 2016, Zhao et al. 2010). There are no significant
4 differences between the two years of the campaign with the only exception of the sampling point
5 *Ca4*, in which a greater amount of Cd was found in 2016, probably for the particular soil pedologic
6 of the field itself. In addition, Cd was totally absent in all *S* samples.
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11 Conversely, As was present in *S* samples with greater concentrations in *S2* (outflow of the farm)
12 and *S6* (outflow of field 3) samples (Table 2b). Moreover, the As average concentration of both
13 years in the porous cups for all the fields investigated was 9.4 ng mL⁻¹. The greatest concentrations
14 of As were found in porous cups *Cb* (in particular in those located in field 3) and in *P2* indicating
15 pre-existing pollution of this area. According to the collected data, it is possible to suggest that As
16 present in surface water (*S1*, the inflow of the farm) is then accumulated by porous cups located at
17 60 cm depth. As it can be deduced from obtained data, it is possible to identify a general water
18 flow direction in the paddy fields from North-West to South-East. This prevailing flow direction
19 contributes to the diffusion of both the nutrients and pesticides.
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29 A comparison between the concentrations of As in the porous cups of dry-seeding and wet-
30 seeding fields is reported in table 4b. The choice of using porous cups is due to the fact that they
31 better show real As concentrations in the fields and in particular the deviations of the
32 concentration values are very closer than those of surface water.
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The biennial average concentrations in *Ca* and *Cb* of dry-seeding fields (1 and 2) were compared with those of wet-seeding ones (3 and 4) through a *t*-test. The table 4 reports the t_{calc} value with the formula above reported, where in this case \bar{x}_1 and \bar{x}_2 are the biennial average concentration value of dry-seeding fields and wet-seeding ones, respectively, n_1 and n_2 are the number of porous cups considered in the fields with the same cultivation method ($n_1=2$ and $n_2=2$), and S_{pooled} is the pooled standard deviation. Therefore, t_{calc} was compared with t_{tab} at 95% of confidence level and with (n_1+n_2-2) degrees of freedom ($t_{\text{tab}(0.05;2)}=2.92$). No significant difference between the two seeding methods were highlighted. In fact, no increment of As concentration in the soil of the two dry-seeding fields (1 and 2) was found and the concentration in the circulating water in the fields was always remained even below the legal limit for the content of As in drinking water ($\leq 10 \mu\text{g L}^{-1}$) (Directive 98/83/EC 1998), exceeded only in a few samples. However, the prolonged anoxic conditions of the fields with wet-seeding have led to greater availability and mobility of As in the circulating water, with its movement along the soil profile (Arao et al. 2009; LaHue et al. 2016,

1 Zhao et al. 2010). In particular, the percolation phenomenon in the field 3 was very intense and
2 very high total As concentrations were found at the great sampling depths. In fact, the water of
3 field 3 is more As-contaminated than the one of field 1, suggesting an accumulating effect due to
4 water flows. Conversely, the increase of As concentration was not observed in the field 4, as the
5 percolation is reduced because of the particular soil characteristics and for the presence of surface
6 stratum that hinders this phenomenon.
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11 As concerns the grain analysis, in 2015, total As concentration was below the limit of 0.20 mg kg⁻¹
12 (Commission Regulation 2006/1881/EC 2006) established by the normative for white rice, but
13 above the limit for the baby food, equal to 0.10 mg kg⁻¹. In particular, a greater amount of total As
14 was detected in grains of the dry-seeding fields (194±20 and 192±20 µg kg⁻¹ for the fields 1 and 2,
15 respectively) than that present in wet-seeding ones (124±13 and 145±15 µg kg⁻¹ for the fields 3
16 and 4, respectively).
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21 In the second year of experiments, the use of the irrigation ditch water with a total As
22 concentration of a magnitude order greater than that of the previous year has resulted in an
23 increase of the total As concentration in the circulating water, especially in the dry-seeding fields.
24 Nevertheless, although greater concentrations have been recorded both in entering and leaving
25 water the fields, there is not a significant accumulation of As in grain, probably due in part to the
26 greater loss due to percolation (Kumarathilaka et al. 2018, LaHue et al. 2016). In all four fields
27 investigated, the total As concentration in grains was lower than the limit allowed by law (0.20 mg
28 kg⁻¹): in particular, greater concentrations were observed in the case of wet-seeding (140±15 µg
29 kg⁻¹ and 137±14 µg kg⁻¹ for the fields 3 and 4 respectively), while the high percolation of As in the
30 soil allowed the two underground sowing to accumulate a smaller quantity of As in grain (81±7 µg
31 kg⁻¹ and 88±8 µg kg⁻¹ for the fields 1 and 2, respectively), equal about less than 39%.
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46 *Development and validation of UHPLC-MS/MS method*

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48 A preliminary MS/MS characterization study of the three herbicides in positive ion mode (PI) was
49 performed in order to identify each analyte fragmentation pattern: each herbicide standard
50 solution (5.0·10⁻² ng mL⁻¹ in methanol) was infused through the syringe pump at 10 µL min⁻¹ into
51 the mass spectrometer. The most intense signals corresponding to the [M+H]⁺ species observed
52 for the herbicides, their two most intense product ions that were used for their quantification and
53 their corresponding structures are reported in Table 5.
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1 For each herbicide a calibration plot reporting the peak area of the most intense transition (y)
2 versus the standard concentration (x) was built, considering 8 concentration levels, ranging from
3 the LOQ value to $2.5 \cdot 10^2$ ng mL⁻¹ (LOQ, $5.0 \cdot 10^{-2}$, $1.0 \cdot 10^{-1}$, 1.0, 10, 50, $1.0 \cdot 10^2$ and $2.5 \cdot 10^2$ ng mL⁻¹,
4 each concentration level replicated three times). The standard solutions were injected in a
5 randomized order to avoid possible memory effects. A 1/x weighted linear regression fit was
6 adopted to interpolate the analyte concentrations. For each calibration curve, an *F*-test was
7 performed to assess whether the models explained a significant fraction of the information
8 present in the measured data. All the F_{calc} were greater than $F_{tab(0.01;1;22)} = 7.94$, therefore the
9 plots explained a significant fraction of the variance present in the data. The three calibration plots
10 were characterized by a good linearity and all R² were greater than 0.9989 (Table 6).

11 Intra- and inter- day precision of the retention times and concentrations were evaluated through
12 the analysis of a standard mixture of the three herbicides ($5.0 \cdot 10^{-2}$ ng mL⁻¹ each), five replicates
13 per day for a week. The obtained results demonstrated that the intra-day relative standard
14 deviation (RSD%) of the concentration was always lower than 4.7% and the inter-day RSD% was
15 always lower than 6.1%. Intra- and inter-day RSD% calculated on the retention time were always
16 lower than 0.6% and 0.7%, respectively (Table 6).

17 Matrix effect (*ME*) results equal to 0 for all the considered analytes, so no relevant ME was found.

18 *Photodegradation studies of the selected herbicides*

19 Two different photoproducts for Ima (P1_Ima and P2_Ima), 3 photoproducts for Pro (P1_Pro,
20 P2_Pro and P3_Pro), while no photodegradation product was identified in Oxa solutions. Previous
21 Oxa degradation products investigations were performed using GC-MS or electroanalytical
22 methods (Boyd-Boland and Pawliszyn 1995; Garrigo et al. 2001; Ishibashi and Suzuki 1988;
23 Kadokami et al. 1991; Kobayashi et al. 1993; Liao et al. 1991; Mattern et al. 1991; Ying and
24 Williams 1999). These approaches led to the identification of degradation products, whose
25 presence was not observed through our LC-MS data.

26 The structures of the degradation products were obtained using the elemental composition, the
27 accurate *m/z*, the number of rings and double bonds (RDBs), the mass error (ppm) and the
28 average MS/MS error (ppm) calculated through the number of MS/MS product ions. The
29 photodegradation products found are reported in Table 7, but they had already been reported in
30 the literature (Harir et al. 2007; Sánchez et al. 2006). Both the Ima degradation products maintain
31 the portion of the molecule characterized by the substituted pyridine ring; in particular, P1_Ima is

1 formed by the opening and subsequent loss of the imidazole ring, while P2_Ima by the opening of
2 the same ring and loss of the amidic group and consequent rearranging of the alkyl chain.

3 Pro degradation products are associated with the preservation of the thiane ring, but they differ
4 for the loss of the O-substituted oxime group and subsequent rearrangement of the remaining
5 structure (P1_Pro and P3_Pro), while P2_Pro is generated by hydroxylation of the
6 hydroxycyclohexenonic ring. It was possible to quantify the concentration (C) of the pesticide still
7 present in the paddy water solutions by mean of the calibration plot. The plot of $\ln C$ versus the
8 degradation time showed a linear behaviour, indicating that all degradation processes follow a
9 first-order reaction. The half-life and the kinetic constants for Ima, Oxa and Pro are reported in
10 Table 8.

11 No contribution of the hydrolysis reaction alone was shown for any pesticide after conservation of
12 their solutions in the dark for a month, at the same concentration of those subjected to
13 photoirradiation.

24 *Paddy water pesticides analysis*

25 The different flooding techniques adopted in the fields did not affect the concentration of the
26 pesticides since they showed similar values in both 2015 and 2016 campaigns.

27 In 2015, the maximum concentration of Ima was 16 ng mL^{-1} , followed by Oxa at 6.0 ng mL^{-1} , and
28 both herbicides were never detected at the end of the 2015 campaign, while Pro was not detected
29 in any sample. In the successive year, no Pro and Oxa were found in all the analyzed samples,
30 while Ima concentration trends were confirmed (as that shows in Fig. 2), and the herbicide
31 concentration remained low around 2.0 ng mL^{-1} at the end of the campaign, indicating a pre-
32 existing contamination of the water, as confirmed by the presence of Ima around at 5.0 ng mL^{-1} in
33 groundwater samples (P1 and P2). Furthermore, the surface water samples showed greater
34 concentration values (maximum values at 24 ng mL^{-1} in correspondence to the Ima application
35 day) than those observed in 2015 (maximum values at 13 ng mL^{-1}). To explain such experimental
36 data, different hypotheses were suggested. The most realistic concerns, again, the pesticide drift:
37 farmers of the surrounding area applied Ima to their crops and, because of the water flow
38 direction the pesticide could have easily reached the area under investigation, increasing its
39 contamination. Another hypothesis can regard the possible leaching of Ima previously retained
40 from the soil.

1 From surface and underground water analysis results, it emerges that the concentration values are
2 strongly dependent on the local treatments in the fields of the herbicide. Irrelevant concentrations
3 of Ima were found in the water leaving the individual fields, while the concentration present in the
4 percolating waters were sometimes high (15-43 g ha⁻¹ in the case of the fields 1 and 2, placed in
5 the summit position with respect to the slope and characterized by coarse substrates), sometimes
6 lower (0-4 g ha⁻¹ in the case of the fields 3 and 4, characterized by lower altitudes and more
7 impermeable soils).
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12 Therefore, it follows that Ima dissipates slowly in medium permeable soils and it persists for a long
13 time in the circulating water, leading to important interactions with the soil as reported by Ball et
14 al. (2003).
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18 Another aspect that has been confirmed is the high degree of pesticide interception on the
19 growing rice leaf area. In fact, in both types of soil and irrigation management, a concentration of
20 Ima always lower in the outlet water has been recorded after the second treatments of the
21 herbicide that was applied with a more developed leaf area compared to the time of the first
22 treatment.
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27 In 2015, relevant Oxa concentrations ranging from 0.030 ng mL⁻¹ to 5.3 ng mL⁻¹ were found in
28 water entering the monitored area and groundwater, even before the application performed by
29 the farmers, indicating a contamination of the area, as reported by the Istituto Superiore per la
30 Protezione e la Ricerca Ambientale (ISPRA) in the National report for the monitoring of pesticides
31 in water (ISPRA 2017) and justifying the limitations imposed by the Management Plan of the
32 Hydrographic District of the Po River and by the National Action Plan for the sustainable use of the
33 Phytosanitary Products of the Lombardy Region. The trends of Oxa concentrations in the surface
34 and groundwater leaving fields seem strongly linked to the contribution of this active principle
35 present in the incoming water during the whole season, while the releases attributable to the
36 locally administered doses are very modest (Fig. 2).
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41 Unlike the kinetics of the three herbicides studied in the lab, the transformation of these
42 pesticides during their applications in fields is influenced by several environmental factors that can
43 also compete with each other (e.g. sunlight, microbial degradation, soil sorption-desorption,
44 leaching and percolation, runoff, ...). The residual Ima concentration is not more significant only
45 after 3 months from its application (<0.1 ng mL⁻¹), nevertheless it is still present its
46 photodegradation product (P2_Ima), that is not possible to quantify because of the unavailability
47 of the standard. In addition, it is not possible to estimate the real persistent time of both Oxa and
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1 Pro in paddy fields, but for different reasons: in the first case, we observe a contamination of the
2 entry water by this pesticide, whereas in the second one the herbicide or its possible degradation
3 products were never detected in any samples.

4 Particular attention was devoted to field 4, in which for both campaigns all the pesticide
5 concentration values were always lower than those found in the others. The explanation could be
6 the particular composition and conformation of the field itself: geomorphologic data showed a
7 slight slope that may facilitate the run-off of the pesticides.

8 To offer a complete overview of paddy water composition, non-target screening was carried out
9 on all the collected samples. The identification of new chromatographic peaks was performed
10 through the help of the dedicated software MasterView™ after setting the restrictive criteria
11 described in Online Resource 3: only the peaks that met all the requirements were automatically
12 included in a list by the software and then extracted from the total ion current (TOF scan). All the
13 samples collected during the campaigns were compared with a blank paddy water sample
14 collected from the same area, before the beginning of the field treatments. Non-target screening
15 is able to find out not only pesticides but also other compounds that could be identified through
16 LC-MS, such as other organic pollutants or characteristic compounds of natural water samples.
17 MasterView™ software was used to explore the samples using, at first, our in-house pesticides
18 database, consisting of the MS/MS spectra of the pesticides previously investigated.

19 The identification of a compound is based on four criteria: retention time (RT), mass accuracy,
20 isotope pattern match and MS/MS library match. As an example, it is reported the workflow used
21 for the tricyclazole (Tcy) identification through the library searching (Fig. 3). The performed direct
22 comparison between the sample and the control showed as significant the signal at m/z 190.0428,
23 to which corresponds the chromatographic peak at RT=3.41 min (Fig. 3A).

24 Thanks to the information on the isotopic pattern of the detected quasi-molecular ion (Fig. 3B)
25 and accurate MS/MS spectrum (Fig. 3C), it was possible to identify the Tcy. As a mirror view, in
26 fact, the library MS/MS spectrum of Tcy (grey trace, Fig. 3C) is reported under the experimental
27 MS/MS spectrum associated to the highlighted m/z signal (blue trace, Fig. 3D), indicating the
28 positive matching between the most abundant fragments, hence the correct attribution of the
29 signal m/z at 190.0428 to Tcy. Such fungicide, used to prevent mycosis in the airborne organs
30 induced by *Piricularia oryzae* (Padovani et al. 2006), was identified in all the collected samples.

31 The presence of Tcy was first confirmed through standard comparison, and then it was included in
32 the developed method and quantified in all the collected samples. Tcy concentration values were
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1 high at the beginning of the campaign (the values in the *Ca* ranged from 0.060 to 13 ng mL⁻¹) and
2 then decreased until the end of it and were lower than LOQs, showing comparable concentration
3 levels for the considered time span. Given the presence of Tcy in all the considered samples, it
4 was also searched for that of its degradation products, whose structures had been elucidated by
5 our group in a previous study (Gosetti et al. 2015), but no degradation products were found. The
6 presence of Tcy was confirmed by the data collected by the local Environmental Protection
7 Agency ARPA (Agenzia Regionale Protezione Ambientale) and ISPRA that identified Tcy in the
8 water samples at the same levels of those found by our analysis, highlighting the ubiquity of this
9 pollutant already present at the beginning of the study.

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11 Another identified pesticide was amidosufuron (Ami), a post-emergence herbicide that inhibits
12 the acetolactate synthase activity involved in the synthesis of some amino acids necessary for
13 weed growth. Ami was identified in the porous cup located at 25 cm deep in field 1, at the end of
14 April. In fact, to protect rice cultivations from cleavers and other broad-leaved weed, Ami has to
15 be applied at an early age, with a height of weed of 3-20 cm.

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17 In addition, other three unknown species U1 at *m/z* 192.1375, U2 *m/z* 263.1390, and U3 *m/z*
18 230.1172 with the elemental compositions of C₁₂H₁₇NO, C₁₄H₁₅NO₂ and C₁₄H₁₈N₂O₃ respectively,
19 were identified in both years.

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21 The three molecular formulas were then searched for in the ChemSpider online database in order
22 to suggest their chemical structures. Figure 4 shows, as an example, the workflow used to identify
23 the chemical structure of U1. U1 *m/z* signal at 192.1375 was extracted from the total ion current
24 (Fig. 4A) as it was considered as significant by the direct comparison between the sample (e.g. the
25 *Ca* sample of field 1 collected 26 June 2015) and the control (blank paddy water sample before
26 the field treatments). The MS (Fig. 4B) and MS/MS (Fig. 4C) spectra were associated with the
27 chromatographic peak at RT=4.44 min (Fig. 4A).

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29 Based on these data, the most plausible elemental formula attributed to U1 was C₁₂H₁₇NO with an
30 accuracy of 0.7 ppm of MS and 15.8 ppm MS/MS data (Table 9). The information obtained was
31 used by MasterView™ to compare the acquired MS/MS spectrum of the U1 with those proposed
32 by the ChemSpider database through an *in-silico* simulation of all the possible chemical structures
33 to which the U1 elemental formula can be associated, considering breaking and rearranging
34 bonds rules (Fig. 4F). The highest matching between the experimental and *in-silico* MS spectra
35 was shown for the N,N-diethyl-meta-toluamide (DEET), ranked first on the list suggested by the
36 software (Fig. 4D).

1 The most abundant fragments gave positive matching with the library ones, confirming the
2 attribution proposed by the software, hence indicating the presence of DEET in the considered
3 sample. DEET is one of the most employed active principles in insect's repellent formulations. Due
4 to its great diffusion, it is considered an emerging contaminant, belonging to the personal care
5 product (PCP) class (Hallè et al. 2015; Zenobio et al. 2015). The maximum concentration of DEET
6 was found in the early summer period.
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10 As concerns U2, since its MS/MS spectrum was not compatible with those *in silico* generated by
11 the structures proposed by ChemSpider, its chemical structure elucidation was based on the
12 elemental composition within a mass tolerance of 1.1 ppm, the isotopic cluster abundance
13 (tolerance of 10%), the number of RDBs, the use of high-accurate and high-resolution MS/MS
14 acquired spectra, from which it was possible to obtain the elemental composition of the product
15 ions (considering an average mass tolerance lower than 7.0 ppm), its retention time plausibility in
16 relation with its calculated Log *P*. In particular, the information obtained through the MS/MS
17 fragmentation are fundamental for the interpretation of the precursor molecular structures. Once
18 the chemical structure of U2 was proposed, it was drawn in PeakView™ where its experimental
19 MS/MS spectrum was compared with that simulated *in silico* for the same structure, giving 96% of
20 matching. The proposed U2 molecular structure is compatible with that of one of the Ima
21 photodegradation products, previously found during the Ima photodegradation (P2_Ima) (Harir et
22 al. 2007).
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26 The correlation between the herbicide and U2 was considered in both campaigns. As an example,
27 Figures 5A and 5B show the trends of Ima and U2 in field 1, considering the *Ca* sampling point in
28 the 2015 campaign. It can be observed how Ima concentration increases not only when field 1 is
29 treated (indicated by the solid red line), but also when the adjacent field 3 is treated (indicated by
30 the dashed yellow line). As time goes by from the date of the field treatment, the concentration
31 of Ima decreases, accompanied by the formation of U2, confirming to be one of the Ima
32 photodegradation products.
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36 On the contrary, for U3 it was not found a positive matching in the ChemSpider database and it
37 was not possible to propose a plausible chemical structure based on the MS/MS fragmentation.
38 However, this species was monitored during both campaigns and comparable profiles were
39 shown. It is interesting to notice that U3 is totally absent in the first 50 days of the campaign and
40 then it starts to increase reaching maximum levels at day 72, keeping constant its level until the
41 end of the investigated period in 2015, corresponding to summer.
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1 In addition, in 2016 campaign it was possible to identify two other unknown compounds, labelled
2 as U4 and U5, whose molecular formulae are $C_{14}H_{25}NO_4$ (m/z 272.1860, PI) and $C_{15}H_{25}N_5O_3$ (m/z
3 324.2024, PI), respectively, but their molecular structures are still under elucidation.

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5 Table 9 summarizes for each pollutant, the elemental composition, the accurate mass, the
6 retention time, the RDB number, the mass error (ppm), and average MS/MS error (ppm)
7 calculated through the number of MS/MS product ions.
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11 Non-target analysis highlighted only the presence of a degradation product of Ima (U2), since real
12 paddy water is an open system, in which different mechanisms take place during the degradation
13 of a pollutant, not only the sunlight or temperature effects but also the effect of soil
14 sorption/desorption and the role of bacteria have to be considered (Gosetti et al. 2018; Polati et
15 al. 2006).
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22 *Achieved advances in the environment and agricultural management during the monitoring*

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24 The changes in the practices adopted in the second year of campaign concerned few variations of
25 all management aspects of rice cultivation (fertilization, water management and phytosanitary
26 treatments). The changes have been made only on a field for each type of rice cultivation (wet-
27 seeding and dry-seeding), whereas the other one was cultivated in the same conditions as those of
28 previous year, in order to preserve as much as possible the rice production from the point of view
29 both of quality and of quantity.
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33 The first objective of this study was the reducing of the nutrient loading, if necessary. As regards
34 nitrogen, it was observed that the pluviometric trend has influenced, especially during the first
35 two months of the growing season, the availability and the loss of this element in the rice field. It
36 has been observed that pre-seeding nitrogenous fertilizations applied at very distant times from
37 the submerged date in the dry-seeding technique can lead to nitrogen losses from the system and
38 to possible risks for groundwater contamination, especially if close to the application of nitrogen
39 fertilizer important rainfall precipitation occurs (as in the year 2015) (Zou et al. 2007). In this case,
40 the use of nitrification inhibitors, as happened in the studied fields, does not always actually allow
41 to mitigate such losses (LaHue et al. 2016). Moreover, it has been ascertained that in both
42 cultivation techniques it is important not to activate a recirculation of the water in the field during
43 the first 10 days from the interventions, as this action leads to a loss of nitrogen in the water
44 coming out of the vents of the field, as well as a deepening of the element along the ground
45 profile with losses due to percolation (LaHue et al. 2016).
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2 At last, the optimal management with autumnal rather than spring burial of straws could allow a
3 better degradation of crop residues and a release of nitrogen useful for plants grown in times of
4 the greatest need (Wang et al. 2016).

5 In the case of potassium, it is important that the fertilization plan takes into account the
6 characteristics of the soil and its potassium content already present, as well as the amount that
7 could be supplied by irrigation and by submerged water. The greater presence of potassium in the
8 circulating water at the beginning of the growing season in both the sowing methods is linked to
9 the contribution of potassium fertilizer in pre-seeding. Moreover, it has to be taken into account
10 also the potassium that is returned by the straw burial and whose release takes place exactly in
11 the initial part of the crop cycle. Therefore, the proper fractionation and the use of applications on
12 the field surface could improve the efficiency of potassic fertilization (Sarkar et al. 2017).

13 The utility of the potassium monitoring is to avoid potassic fertilizations where there is already a
14 high quantity of the element deriving from the irrigation.

15 For example, in 2016, the potassium intake deriving from the submerged water of the fields
16 managed with the two sowing techniques was very high, so as to trigger a considerable loss of this
17 nutrient both from the outlets and from percolation along the soil profile. In this case, the high
18 quantity of potassium deriving from the water of the irrigation ditch could actually allow to
19 reduce, or completely eliminate, the quantity of potassium for the treatment in the field.

20 The second objective of the study was the reduction of As and Cd content in rice grain. The As
21 concentration in the circulating water has shown some differences between the two years of the
22 study, particularly influenced by the chemical composition of the inflow water of the irrigation
23 ditch used for the submersion of the paddy fields (*Ca3* in Table 1b and *S1, S2, S3* in Table 2b). In
24 order to evaluate how a different water management can have an influence on the accumulation
25 of this element in grain, it was decided to adopt in the field 1, a dry period from the steam
26 elongation (in the last week of July) up to the booting (in the first week of August) with the aim of
27 reducing the As migration into the grain. This further expedient allowed a slight reduction of total
28 As in grain compared to the control field 2, although the difference was not very significant. Also
29 as concerns the Cd concentration, it is kept under control: the average measured amount in the
30 grain was of 20 $\mu\text{g kg}^{-1}$ in the fields cultivated with the technique of dry-seeding, while with that of
31 wet-seeding the quantities never exceed 5 $\mu\text{g kg}^{-1}$, being the limit much higher (0.20 mg kg^{-1})
32 (Commission Regulation 2006/1881/EC 2006).

1 The third objective was the evaluation of the differences between dry-seeding and wet-seeding
2 techniques, but no significant difference was highlighted (Table 4). The literature reports
3 discordant opinions about the alternate wetting and dry irrigations: some studies report that this
4 irrigation type reduces total cumulative plant N (Zou et al. 2007), but other ones report exactly the
5 contrary (Zhang et al. 2008, 2009a, Wang et al. 2011). A recent study reports that the adoption of
6 an alternate wetting and moderate drying can be the best compromise as concerns the grain yield
7 (Wang et al. 2016), whereas another study indicates that the imposition of a single soil drying
8 period can mitigate As accumulation in rice grain, but it depends on the severity and timing of the
9 drying period (Carrijo et al. 2019).

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17 As concerns the degradation of pesticides and the permanence time in the field, some
18 considerations are here reported. In general, we can observe that the pesticides reached their
19 maximum concentrations one day after the administration (indicated as an example in Fig. 2 by
20 the solid red line) and in the day after the application of the same pesticide in the adjacent field
21 (indicated as an example in Fig. 2 by the dashed yellow line). This may be due to the pesticides
22 drift following the water flow: in fact the herbicides may fall directly onto the crops of the
23 surrounding fields not only due to the speed and direction of the wind, and to the aspects related
24 to their distribution mode (diameter of the sprayed drops, pressure of the sprayer, distance
25 between the crop and the nozzles, type and orientation of the nozzles) but also to the direction of
26 the water flow, which is directed from North-West towards South-East in the considered paddy
27 area.

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38 The degradation time of the three herbicides were studied simulating sunlight irradiation and
39 ranged from 1.05 to 5.37 h (Table 8), but as it can be shown in Fig. 2 in the case of the Ima, the
40 real persistence time of this herbicide after its application in the field has to be correlated to many
41 other environmental factors (e.g. runoff, soil sorption, soil composition, percolation and leaching
42 phenomena, and microbial degradation). Therefore, an Ima concentration under 0.1 ng mL^{-1} was
43 found only after 3 months of the applications in the field, in which remains the degradation
44 product P2_Ima. Furthermore, the couple of compounds constituted by Ima and P2_Ima was
45 adopted as a tracer to support fluid dynamic and stratification data of the fields showed before.
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48 Pro was never detected in the fields and therefore no data about its permanence time can be
49 given. For what regards Oxa, it was not possible to correctly estimate the permanence time
50 because of the continuous but different contribution of this herbicide from the entry water of the
51 farm and from adjacent farms.

1 Since quite significant values of the Ima pesticide were detected in 2015 during the period
2 immediately following its application in the field and in that adjacent, with the aim of reducing the
3 spread of this pesticide in surface water, in the agricultural campaign 2016 it was decided to keep
4 closed the outlets of the field for 5-6 days after treatment. However, this precaution did not bring
5 the desired results, as probably it was not sufficient to limit the diffusion of Ima in surface water.
6
7 Therefore, it is possible for these herbicides to confirm how the application protocols due to good
8 agricultural practice, which consist in respecting the time of re-introducing the water after
9 treatment and the closure of discharges for some days of the treated fields, allow to reduce to
10 minimum spread of the pesticide and of their transformation products in the surrounding
11 environment.
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13 In addition, the identification of photodegradation products of the studied pesticides together
14 with the finding of untarget compounds in water gave the possibility to expand the methods of
15 investigation.
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27 **Conclusions**

28 The results indicated that the quality of the water bodies used in paddy fields meets the Italian
29 and European water quality criteria for agricultural use (Directive 2000/60/EC 2000; Italian
30 Legislative Decree 152/06 2006).
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34 Pre-seeding nitrogenous fertilization applied at very distant time from the submersion of the field
35 and the activation of the recirculation in the field during the first 10 days from the application lead
36 to the loss of nutrients, in particular N. A correct water management, followed by a control of K
37 concentration in the entry water allows avoiding potassic fertilization where there is an excess of
38 this nutrient.
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44 No significant difference was found neither on the As and Cd nor pesticides concentrations
45 between dry-seeding and wet-seeding techniques. However, a slight reduction of total As in grain
46 was obtained adopting a dry period from the steam elongation up to booting.
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50 The concentrations of the three widely used herbicides (Ima, Oxa and Pro) were determined by LC-
51 MS/MS: the maximum concentrations of Ima, Oxa and Pro were found on the day following the
52 corresponding treatment and the day after the same treatment on the adjacent field. Although
53 the photodegradation half-time of these pesticides simulated in paddy water ranged from 1.05 to
54 5.37 h, the real degradation conditions are enough different because other environmental factors
55 are involved. It is possible to estimate a concentration $<0.1 \text{ ng mL}^{-1}$ of Ima in the water only after
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1 three months from the application and an increasing formation of a photodegradation product
2 (P2_Ima). It is not possible to give the permanence time of Oxa and Pro: in the first case, there is a
3 continuous but different contribution of Oxa arriving from entry water of the farm or from
4 adjacent farms, in the second case the herbicide was never quantified in any samples.
5

6 Unlikely from the simulated photodegradation study in which two degradation products for Ima
7 and three for Pro were found, only the P2_Ima was identified in the real samples.
8

9 Furthermore, non-target screening allowed the identification of Tcy, Ami, and the emerging
10 contaminant DEET. In addition, other three species were identified in 2015 (U3) and 2016 (U4 and
11 U5) campaigns, but their structures are still under elucidation.
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13 The low number of pollutant species found in the analyzed paddy water samples associated with
14 the good water quality parameters found in the outflows of paddy fields indicates that controlled
15 and correct agronomics practices do not contribute to increase the environmental pollution, but
16 that paddy fields can be used to reduce the loaded polluting species.
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Caption to figures

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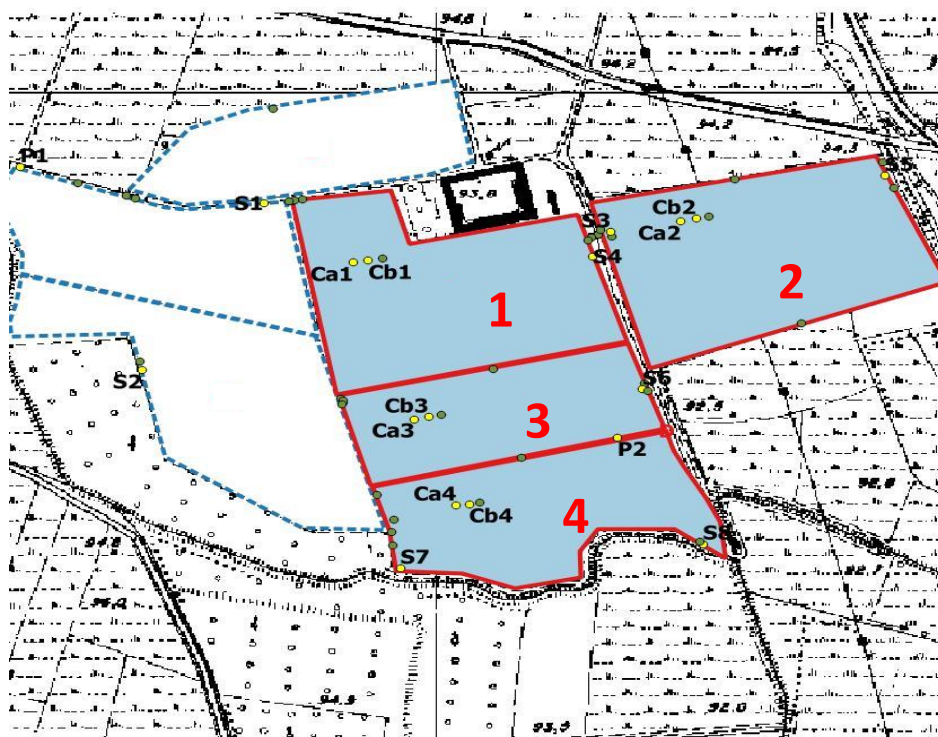
Fig. 1. Paddy fields (indicated with numbers) and sampling points (indicated with *S* for surface water, *P* for underground water, *Ca* and *Cb* for porous cups at 25 cm and 60 cm of depth, respectively) considered in the monitored area.

Fig. 2. Imazamox and oxadiazon concentration trends in the field 1 in 2015, considering the samples collected from the porous cup at 25 cm depth (*Ca1*).

Fig. 3. Extracted ion chromatogram (A), isotopic pattern (B), accurate MS/MS spectrum (C) of the signal at m/z 190.0428 and the library matching with tricyclazole MS/MS spectrum (D).

Fig. 4. Information used to identify the chemical structure of N,N-diethyl-meta-toluamide (DEET). Extracted ion chromatogram of m/z 192.1375 (PI) (A), isotopic pattern (B), accurate MS/MS spectrum (C), the ChemSpider database suggested name (D), the proposed chemical structure (E) and the positive matching between the experimental MS/MS spectrum and that simulated *in silico* (F).

Fig. 5. Ima concentration trend (A) and U2 (P2_Ima) profile (B) in field 1, considering the sample collected from the porous cup at 25 cm of depth (*Ca1*). The treatments applied on field 1 are indicated by the solid red line, while those applied to the adjacent field 3 are indicated by the dashed yellow line.



Sampling Points

Surface water (S1-S8)

- S1: inflow of the farm
- S2: outflow of the farm
- S3: inflow of the field 2
- S4: outflow of the field 1
- S5: outflow of the field 2
- S6: outflow of the field 3
- S7: outflow of the field 4
- S8: outflow of the field 4

Underground water

- P1: upstream piezometer
- P2: downstream piezometer

Porous cups

- Ca: 25 cm soil depth
- Cb: 60 cm soil depth

Fig. 1

Figure 2

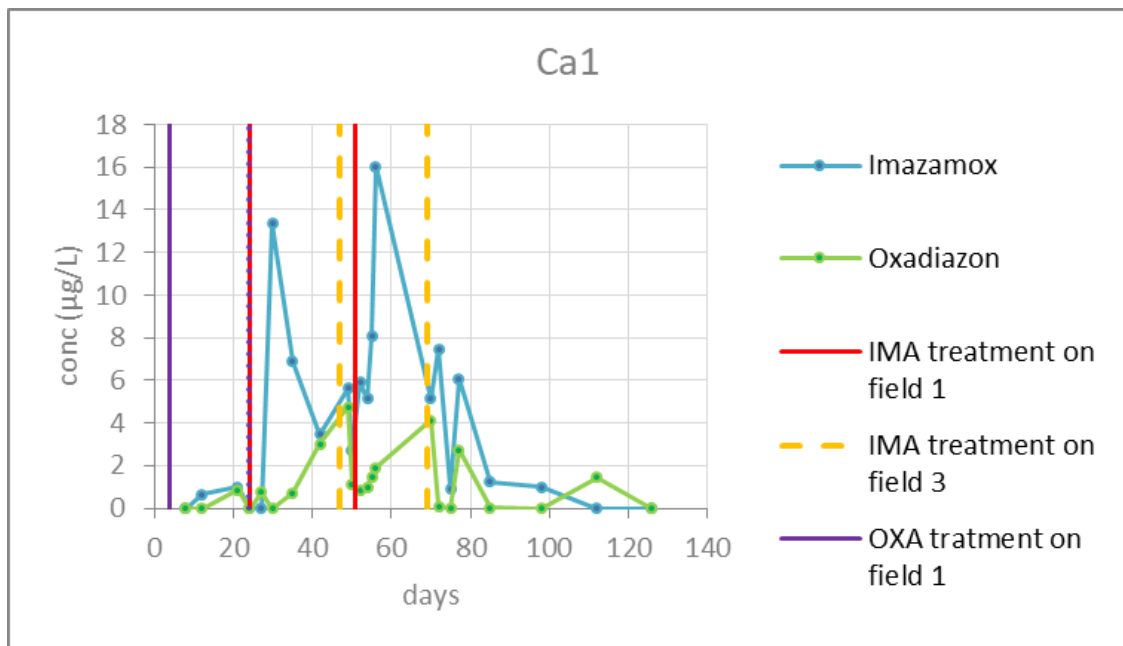


Fig. 2

Figure 3

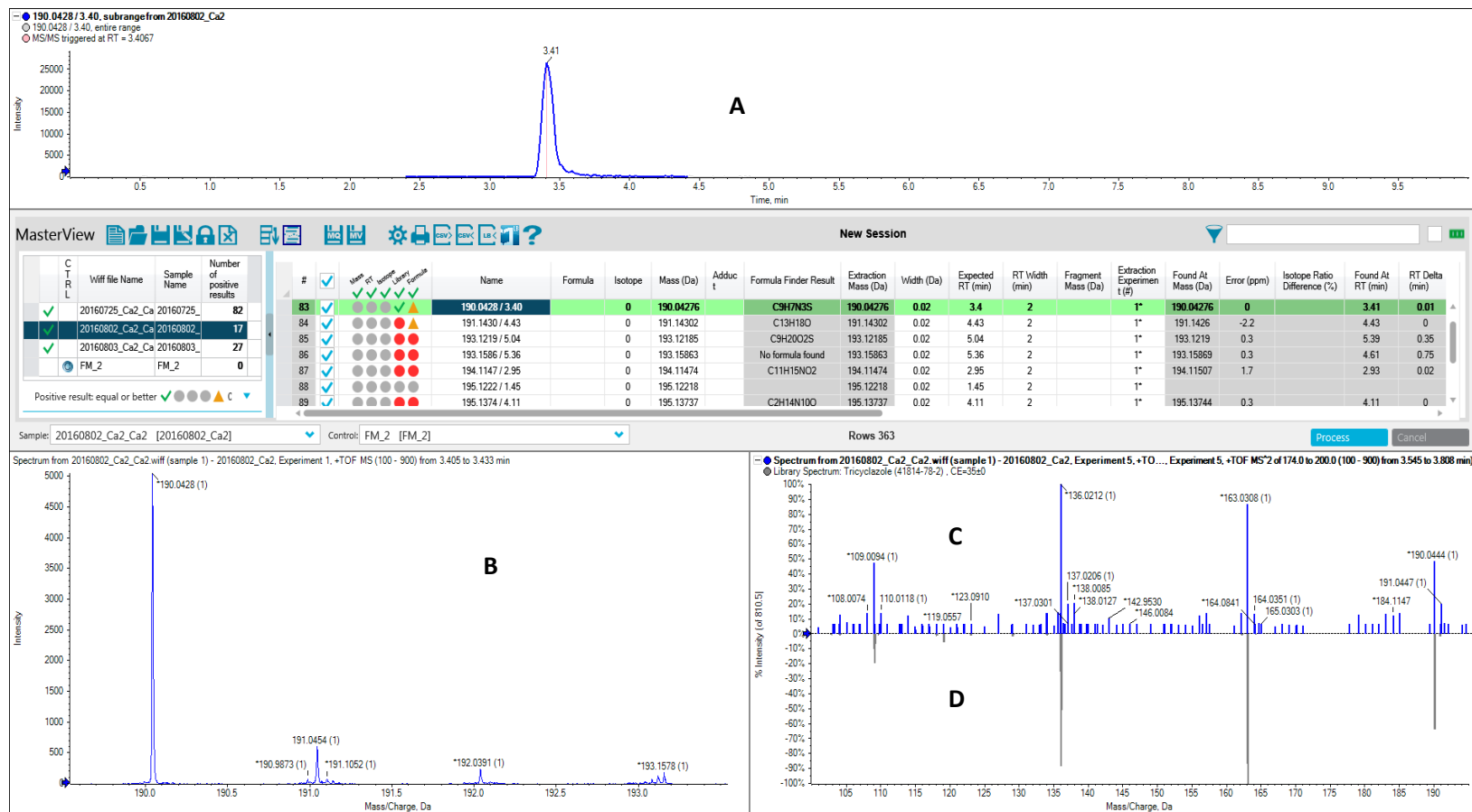


Fig. 3.

Figure 4

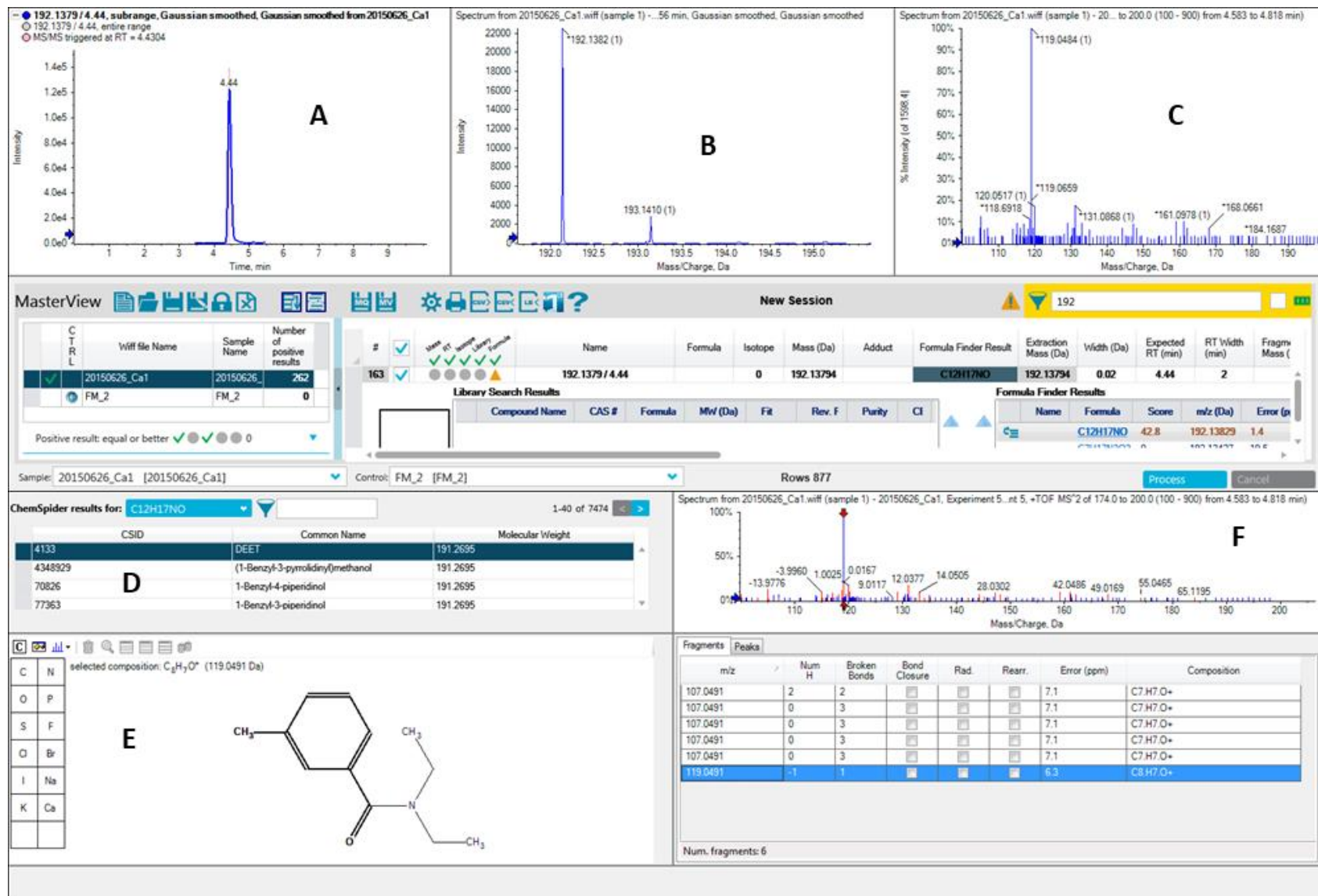


Fig. 4

Figure 5

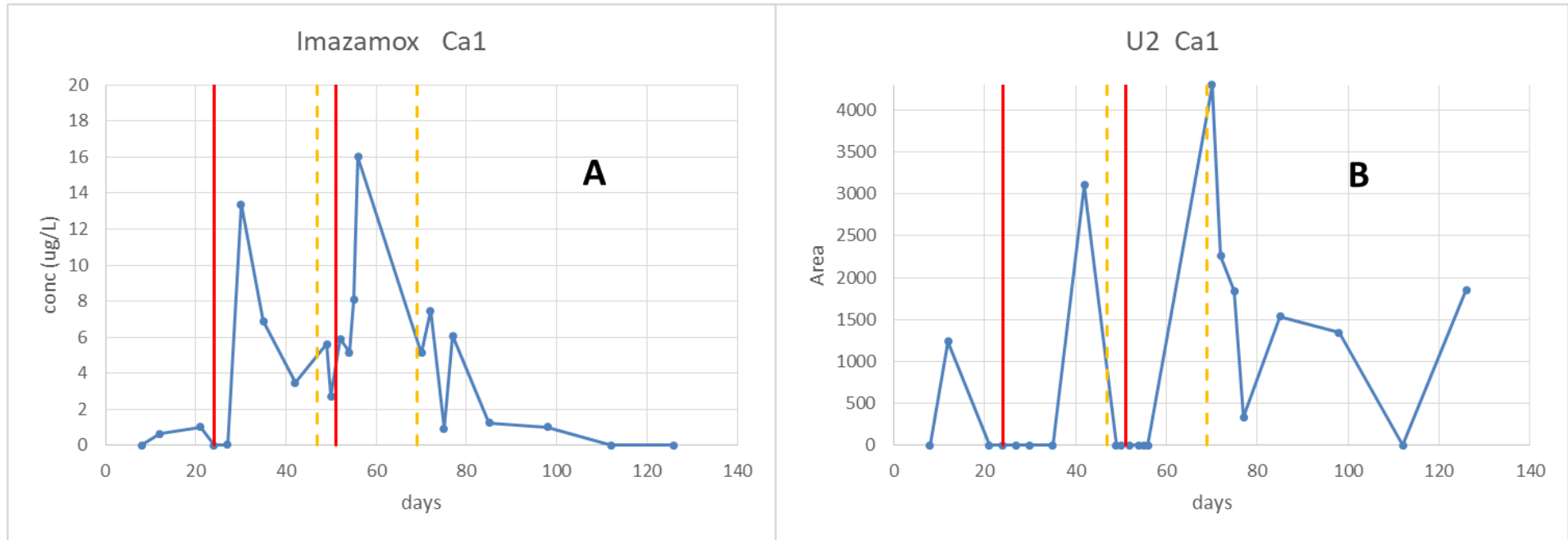


Fig. 5

Table 1

Sample		N (mg L ⁻¹)			P (ng mL ⁻¹)			K (mg L ⁻¹)		
		2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}
P1	min	1.7	1.8		n.d.	4.2		0.6	0.7	
	max	4.0	11.2		61	95 ·10		1.4	91.3	
	mean	2.6 ± 0.8	5.3 ± 3.6	1.77	25 ± 26	(13 ± 28) ·10	0.963	0.89 ± 0.33	13.3 ± 24.0	1.26
P2	min	1.0	0.5		n.d.	4.0		0.3	0.4	
	max	2.7	22.4		92	11 ·10		2.1	42.2	
	mean	1.8 ± 0.7	7.2 ± 7.3	1.79	35 ± 42	(11 ± 16) ·10	1.13	0.9 ± 0.6	8.4 ± 11.3	1.61
Ca1	min	2.2	0.5		27.5	11		5.6	1.2	
	max	19.8	15.3		61 ·10	74 ·10		19.2	59.6	
	mean	7.0 ± 6.7	5.2 ± 5.6	0.554	(25 ± 22) ·10	(14 ± 22) ·10	0.515	11.8 ± 5.2	12.8 ± 17.2	0.138
Ca2	min	1.1	2.5		n.d.	0.68		3.8	0.5	
	max	22.6	13.8		52	17 ·10		22.4	76.5	
	mean	7.3 ± 8.8	7.1 ± 4.8	0.0412	22 ± 21	(49 ± 72) ·10	1.60	8.9 ± 7.0	17.2 ± 26.2	1.20
Ca3	min	1.0	0.7		n.d.	23		1.5	3.0	
	max	7.2	14.0		21 ·10	24 ·10		6.2	144.9	
	mean	3.6 ± 2.9	7.2 ± 5.1	1.56	66 ± 97	93 ± 80	0.547	3.3 ± 2.0	32.3 ± 47.0	1.29
Ca4	min	1.1	0.8		n.d.	4.2		4.5	0.57	
	max	3.3	14.6		62	19 ·10		7.5	82.2	
	mean	1.8 ± 0.9	6.2 ± 6.0	1.78	16 ± 27	68 ± 84	1.47	3.0 ± 3.0	22.0 ± 29.3	1.23
Cb1	min	2.6	1.2		n.d.	0.52		1.0	0.2	
	max	16.4	7.8		63	15 ·10 ²		6.0	27.9	
	mean	5.8 ± 5.4	5.2 ± 2.5	0.276	13 ± 25	(22 ± 48) ·10	1.05	2.5 ± 1.8	7.7 ± 8.2	1.36
Cb2	min	1.8	0.5		n.d.	6.0		3.6	0.7	
	max	16.3	8.4		34 ·10	27 ·10		16.6	37.2	
	mean	6.8 ± 6.8	4.1 ± 2.9	0.966	85 ± (13 ·10)	(75 ± 83) ·10	0.167	9.0 ± 5.1	9.9 ± 12.8	1.06
Cb3	min	3.6	0.5		n.d.	5.8		1.4	0.6	
	max	7.9	7.4		10 ·10	19 ·10		3.6	68.6	
	mean	5.6 ± 1.7	5.5 ± 2.6	0.0597	19 ± 42	(62 ± 74) ·10	1.25	2.7 ± 0.8	12.8 ± 19.2	1.44
Cb4	min	2.1	0.5		n.d.	1.6		1.1	0.4	
	max	2.7	7.5		87	13 ·10 ²		3.3	75.1	
	mean	2.1 ± 0.2	4.3 ± 2.7	1.72	36 ± 35	(21 ± 49) ·10	0.856	2.5 ± 0.8	12.4 ± 22.3	1.09

Table 1a: Total N, P, K concentrations in underground water samples (P1 and P2) and porous cups (Ca1, Ca2, Ca3, Ca4, Cb1, Cb2, Cb3, Cb4). The minimum, the maximum and the year average value for each sampling point have been reported. The average values of two years have been compared through a t-test at 95% confidence level ($t_{\text{tab}(0.05, 11)}=1.80$). *t*_{calc} is reported in bold when the test is significative.

Sample		As (ng mL ⁻¹)			Cd (ng mL ⁻¹)		
		2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}
P1	min	4.0	2.7		n.d.	0.010	
	max	22.1	36.5		0.0053	0.91	
	mean	11.0 ± 7.1	10.7 ± 11.7	0.0642	(9 ± 22) · 10 ⁻⁴	0.22 ± 0.32	1.66
P2	min	0.5	2.7		n.d.	0.006	
	max	0.9	46.7		0.21	0.273	
	mean	0.7 ± 0.2	11.0 ± 15.9	1.57	(59 ± 79) · 10 ⁻³	0.11 ± 0.11	1.00
Ca1	min	2.7	2.6		n.d.	0.01	
	max	15.0	33.6		1.1	1.52	
	mean	7.2 ± 4.3	14.3 ± 14.1	1.17	0.30 ± 0.44	0.33 ± 0.59	0.0959
Ca2	min	1.0	1.6		n.d.	n.d.	
	max	5.3	29.2		0.71	0.65	
	mean	2.9 ± 1.5	11.0 ± 11.8	1.64	0.22 ± 0.29	0.23 ± 0.25	0.119
Ca3	min	1.0	1.0		0.012	0.004	
	max	4.6	13.1		0.12	0.21	
	mean	3.1 ± 1.3	7.7 ± 4.7	2.29	0.049 ± 0.052	0.097 ± 0.091	1.13
Ca4	min	0.6	1.6		n.d.	0.002	
	max	10.5	32.6		0.15	0.459	
	mean	5.7 ± 4.2	12.8 ± 11.0	1.48	0.031 ± 0.065	0.19 ± 0.19	1.98
Cb1	min	0.8	2.7		n.d.	0.012	
	max	10.0	31.5		0.14	0.732	
	mean	4.8 ± 4.2	9.7 ± 10.8	1.04	0.053 ± 0.061	0.26 ± 0.33	1.51
Cb2	min	0.7	1.1		n.d.	0.033	
	max	8.3	25.9		0.18	0.492	
	mean	4.4 ± 3.0	11.4 ± 9.0	1.78	0.047 ± 0.071	0.16 ± 0.19	1.37
Cb3	min	3.4	1.2		n.d.	0.010	
	max	55.7	32.4		0.05	0.473	
	mean	26.7 ± 20.3	13.8 ± 10.7	1.46	0.0083 ± 0.0204	0.14 ± 0.20	1.70
Cb4	min	1.3	1.0		n.d.	0.01	
	max	10.3	17.5		0.20	0.67	
	mean	7.0 ± 3.4	7.5 ± 6.4	0.159	0.046 ± 0.087	0.21 ± 0.23	1.63

Table 1b: Total As and Cd concentrations in underground water samples (*P1* and *P2*) and porous cups (*Ca1*, *Ca2*, *Ca3*, *Ca4*, *Cb1*, *Cb2*, *Cb3*, *Cb4*). The minimum, the maximum and the year average value for each sampling point have been reported. The average values of two years have been compared through a *t*-test at 95% confidence level ($t_{\text{tab}(0.05, 11)}=1.80$). t_{calc} is reported in bold when the test is significant.

Table 2

Sample		N (mg L ⁻¹)			P (ng mL ⁻¹)			K (mg L ⁻¹)		
		2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}
S1	min	1.2	1.4		66	7		0.5	0.1	
	max	2.0	7.6		70	518		3.5	53.8	
	mean	1.7 ± 0.3	4.3 ± 2.7	2.31	67.3 ± 2.0	(20 ± 19) · 10	1.689	1.6 ± 1.2	12 ± 16	1.62
S2	min	1.2	2.2		67	0.3		0.48	0.5	
	max	2.7	11.2		72	609.5		3.6	35.3	
	mean	2.0 ± 0.6	5.7 ± 3.3	2.64	70.1 ± 1.6	(15 ± 23) · 10	0.838	1.7 ± 1.3	12.3 ± 11.3	2.28
S3	min	1.2	1.4		33.8	23		0.6	1.4	
	max	2.0	77		44.6	129		3.6	13.2	
	mean	1.7 ± 0.4	15 ± 27	1.18	39. ± 7.6	76 ± 52	1.71	1.7 ± 1.2	6.2 ± 4.8	2.23
S4	min	1.2	1.6		124	8		0.6	0.9	
	max	17	5.7		282	134		22.4	10.7	
	mean	4.4 ± 6.2	3.3 ± 1.6	0.456	171 ± 57	71 ± 89	2.37	6.5 ± 8.5	5.8 ± 6.9	0.175
S5	min	1.5	0.5		91	52		0.7	6.2	
	max	12.6	7.4		114	968		32.7	183.7	
	mean	4.0 ± 4.2	3.7 ± 2.2	0.154	99 ± 11	510 ± 648	1.54	7.2 ± 12.5	(9 ± 12) · 10 ²	1.70
S6	min	1.0	0.6		8	13		0.6	0.8	
	max	3.0	5.8		198	193		4.5	15.6	
	mean	1.6 ± 0.7	3.1 ± 2.0	1.72	142 ± 72	67 ± 74	1.87	2.5 ± 1.5	5.7 ± 6.7	1.12
S7	min	1.3	2.8		5	59		0.7	0.8	
	max	22.5	7.9		62	2315		6.9	26.3	
	mean	5.1 ± 8.5	4.7 ± 1.8	0.126	30 ± 25	(6 ± 11) · 10 ²	1.47	2.4 ± 2.4	17 ± 10	3.57
S8	min	1.1	0.5		7	51		1.5	0.6	
	max	1.6	8.4		68	371		4.4	23.6	
	mean	1.3 ± 0.2	3.3 ± 2.7	1.77	31 ± 27	(15 ± 15) · 10 ²	1.92	3.0 ± 1.2	10.3 ± 8.0	2.20

Table 2a: Total N, P, K concentrations in surface water samples (S1, S2, S3, S4, S5, S6, S7 and S8). The minimum, the maximum and the year average values for each sampling point have been reported. The average values of two years have been compared through a *t*-test at 95% confidence level ($t_{\text{tab}(0.05, 11)}=1.80$). t_{calc} is reported in bold when the test is significant.

Sample		As (ng mL ⁻¹)			Cd (ng mL ⁻¹)		BOD ₅ (mg L ⁻¹)			TSS (mg L ⁻¹)		
		2015	2016	<i>t</i> _{calc}	2015	2016	2015	2016	<i>t</i> _{calc}	2015	2016	<i>t</i> _{calc}
S1	min	0.2	0.7				4.0	1.0		5	5	
	max	1.4	24.1				5.0	4.5		56	48	
	mean	0.8 ± 0.9	8.2 ± 8.5	2.11	n.d.	n.d.	4.2 ± 0.4	2.8 ± 1.6	2.01	41 ± 19	25 ± 16	1.67
S2	min	n.d.	2.6				4.9	1.0		15	2	
	max	n.d.	11.4				6.6	9.3		42	77	
	mean	n.d.	8.4 ± 3.0	6.71	n.d.	n.d.	5.6 ± 0.7	3.9 ± 2.7	1.51	32 ± 10	30 ± 31	0.167
S3	min	0.05	n.d.				4.0	1.4		12	9	
	max	1.6	n.d.				6.8	6.2		42	44	
	mean	0.8 ± 0.7	n.d.	2.66	n.d.	n.d.	5.3 ± 1.4	3.5 ± 1.8	2.03	27 ± 13	22 ± 13	0.539
S4	min	3.6	n.d.				4.0	1.0		6	4	
	max	11.7	33.0				6.6	2.0		46	42.6	
	mean	6.7 ± 4.3	5 ± 12	0.258	n.d.	n.d.	5.2 ± 1.0	1.5 ± 0.71	7.62	25 ± 18	19 ± 16	0.577
S5	min	n.d.	n.d.				4.0	2.5		18	9	
	max	6.9	28.6				5.8	6.8		48	49.9	
	mean	2.2 ± 3.5	5 ± 10	0.732	n.d.	n.d.	4.7 ± 0.7	4.4 ± 2.2	0.304	30 ± 11	27 ± 13	0.333
S6	min	n.d.	n.d.				4.0	1.5		5	7.5	
	max	10.5	35.3				5.0	36		49	133.5	
	mean	4.4 ± 4.6	10 ± 14	0.985	n.d.	n.d.	4.4 ± 0.5	8.1 ± 12.4	0.729	23 ± 19	41 ± 34	1.24
S7	min	n.d.	n.d.				4.0	1		14	2	
	max	3.9	31.5				6.6	10		64	104	
	mean	1.6 ± 1.7	9 ± 13	1.46	n.d.	n.d.	5.1 ± 0.9	4.4 ± 3.1	0.537	36 ± 19	32 ± 20	0.341
S8	min	1.4	n.d.				4.0	1		7	3	
	max	4.8	11.5				7.0	21.67		115	100	
	mean	2.6 ± 1.2	4.7 ± 4.4	1.11	n.d.	n.d.	4.7 ± 1.2	5.0 ± 7.4	0.0931	57 ± 41	40 ± 39	0.739

Table 2b: Total As and Cd concentrations, BOD₅ and TSSs in surface water samples (S1, S2, S3, S4, S5, S6, S7 and S8). The minimum, the maximum and the year average values for each sampling point have been reported. The average values of two years have been compared through a *t*-test at 95% confidence level (*t*_{tab(0.05, 11)}=1.80). *t*_{calc} is reported in bold when the test is significant.

Sample		Total Hardness (mg L ⁻¹ as CaCO ₃)	COD (mg L ⁻¹)	Anionic Surfactants (mg L ⁻¹)
		2015	2015	2015
S1	min	12.5	20	<0.05
	max	19.2	60	<0.05
	mean	16.6 ± 3.0	36 ± 15	<0.05
S2	min	13.7	24	<0.05
	max	20.7	41	<0.05
	mean	18.1 ± 2.9	34 ± 8	<0.05
S3	min	13.3	26	<0.05
	max	20.5	50	<0.05
	mean	17.0 ± 3.1	36 ± 11	<0.05
S4	min	13.4	23	<0.05
	max	25.0	44	<0.05
	mean	17.9 ± 4.1	34 ± 7	<0.05
S5	min	13.3	24	<0.05
	max	19.3	41	<0.05
	mean	16.7 ± 2.2	34 ± 7	<0.05
S6	min	25.5	21	<0.05
	max	32.4	77	<0.05
	mean	28.6 ± 2.0	39 ± 19	<0.05
S7	min	16.4	21	<0.05
	max	26.0	46	<0.05
	mean	19.8 ± 3.4	33 ± 10	<0.05
S8	min	24.2	20	<0.05
	max	30.7	130	<0.05
	mean	28.2 ± 3.4	63 ± 10	<0.05

Table 2c: Total hardness, COD and anionic surfactant concentrations in surface water samples (*S1, S2, S3, S4, S5, S6, S7 and S8*). The minimum, the maximum and the average values of 2015 year for each sampling point have been reported.

Element	LOD (ng mL ⁻¹)	LOQ (ng mL ⁻¹)
Ag	27·10 ⁻⁴	90·10 ⁻⁴
Al	1.1	3.8
As	48·10 ⁻³	16·10 ⁻²
Au	11·10 ⁻¹	35·10 ⁻¹
B	17·10 ⁻¹	57·10 ⁻¹
Ba	38·10 ⁻³	13·10 ⁻²
Cd	33·10 ⁻⁴	11·10 ⁻²
Co	60·10 ⁻⁵	20·10 ⁻⁴
Cr	15·10 ⁻³	51·10 ⁻²
Cs	30·10 ⁻⁵	10·10 ⁻⁴
Cu	20·10 ⁻¹	67·10 ⁻¹
Fe	6.3	21
Hg	77·10 ⁻³	26·10 ⁻²
Ho	24·10 ⁻⁴	79·10 ⁻³
Ir	26·10 ⁻⁴	85·10 ⁻³
K	26·10 ⁻⁴	85·10 ⁻³
Lu	11·10 ⁻⁴	35·10 ⁻³
Mn	61·10 ⁻³	20·10 ⁻²
Mo	40·10 ⁻³	13·10 ⁻²
Ni	54·10 ⁻³	18·10 ⁻²
P	4.1	14
Pb	86·10 ⁻⁴	29·10 ⁻³
Pd	38·10 ⁻⁴	13·10 ⁻³
Pt	42·10 ⁻³	14·10 ⁻²
Rb	15·10 ⁻³	51·10 ⁻²
Rh	30·10 ⁻⁵	10·10 ⁻⁴
Sb	61·10 ⁻⁴	20·10 ⁻³
Se	1.4	4.7
Sn	18·10 ⁻³	61·10 ⁻²
Tb	59·10 ⁻⁴	20·10 ⁻³
Tl	50·10 ⁻⁵	17·10 ⁻⁴
V	40·10 ⁻³	13·10 ⁻²
Zn	3.3	11

Table 13. LOD and LOQ values of ICP-MS method.

Sample	N (mg L ⁻¹)			P (ng mL ⁻¹)			K (ng mL ⁻¹)		
	Dry-seeding	Wet-seeding	<i>t</i> _{calc}	Dry-seeding	Wet-seeding	<i>t</i> _{calc}	Dry-seeding	Wet-seeding	<i>t</i> _{calc}
Ca	6.6 ± 0.8	4.7 ± 1.0	2.17	227 ± 42	101 ± 83	0.876	12.7 ± 0.5	15.2 ± 3.7	1.91
Cb	5.42 ± 0.03	4.4 ± 1.5	0.886	98 ± 26	81 ± 58	1.51	7.3 ± 3.1	7.6 ± 0.2	2.41

Table 4a: Total N, P, and K concentrations in porous cups (*Ca* and *Cb*). The year average values for the cups of the fields 1 and 2 (dry-seeding) and of the fields 3 and 4 (wet-seeding) have been reported. The average values of two different type of seedings have been compared through a *t*-test at 95% confidence level ($t_{\text{tab}(0.05, 2)}=2.92$). No *t*_{calc} value is significant.

Sample	As (mg L ⁻¹)			Cd (ng mL ⁻¹)		
	Dry-seeding	Wet-seeding	<i>t</i> _{calc}	Dry-seeding	Wet-seeding	<i>t</i> _{calc}
Ca	8.8 ± 2.7	7.3 ± 2.7	0.560	0.27 ± 0.06	0.13 ± 0.04	2.66
Cb	7.6 ± 0.5	13.8 ± 9.2	0.960	0.13 ± 0.04	0.10 ± 0.03	0.772

Table 4b: As and Cd concentrations in porous cups (*Ca* and *Cb*). The year average values for the cups of the fields 1 and 2 (dry-seeding) and of the fields 3 and 4 (wet-seeding) have been reported. The average values of two different type of seedings have been compared through a *t*-test at 95% confidence level ($t_{\text{tab}(0.05, 2)}=2.92$). No *t*_{calc} value is significant.

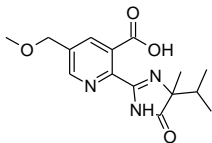
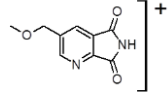
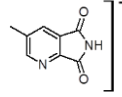
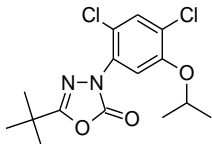
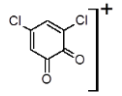
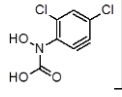
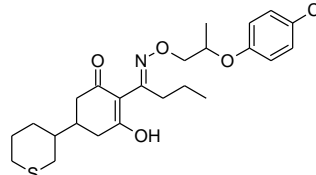
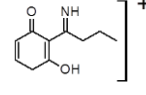
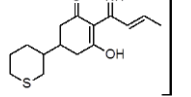
Analyte	[M+H] ⁺	Product ion (m/z)	RT (min)	Proposed product ion structure
Imazamox (Ima)	 306.1	193.0612	3.2	
		163.0497		
Oxadiazon (Oxa)	 345.1	176.9504	6.1	
		219.9559		
Profoxydim (Pro)	 466.2	180.1025	5.9	
		280.1381		

Table 25: Quasi-molecular ion species of the three pesticides, their most intense product ions, their structures and retention times (RT).

Analyte peak name	LOD (ng mL ⁻¹)	LOQ (ng mL ⁻¹)	Linearity range (ng mL ⁻¹)	R ²	RSD% intra day (n=5) t _R	RSD% inter day (n=35) t _R	RSD% intra day (n=5) (conc)	RSD% inter day (n=35) (conc)	Recovery (%)
Imazamox	40·10 ⁻³	13·10 ⁻²	LOQ-2.5·10 ²	0.9998	0.6	0.7	4.7	6.1	99.2 ± 0.9
Oxadiazon	50·10 ⁻³	17·10 ⁻²	LOQ-2.5·10 ²	0.9995	0.2	0.2	2.4	2.7	98.7 ± 1.0
Profoxydim	40·10 ⁻³	13·10 ⁻²	LOQ-2.5·10 ²	0.9989	0.2	0.5	2.0	2.3	100.9 ± 1.5
Tricyclazole	40·10 ⁻³	13·10 ⁻²	LOQ-2.5·10 ²	0.9991	0.1	0.2	1.8	3.1	101.2 ± 1.1

Table 36: Linearity range, regression coefficient (R²), LOD, LOQ, intra- and inter-day RSD (%) of retention time and of concentration and average recovery of each analyte.

Table 7

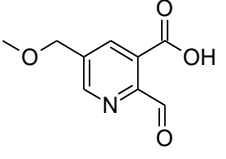
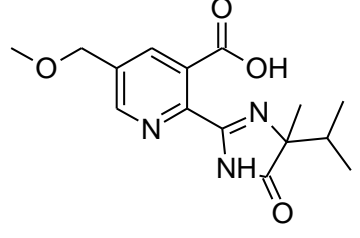
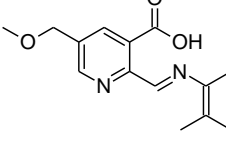
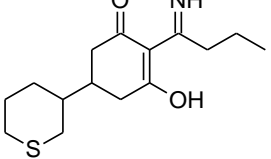
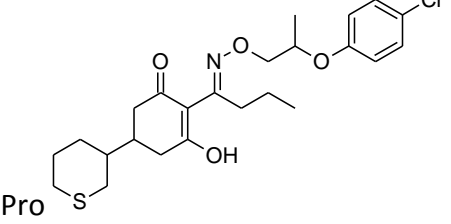
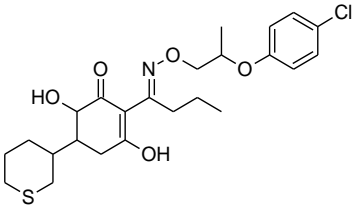
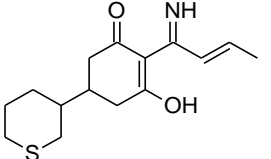
	[M+H]⁺ species	Precursor herbicide	Molecular formula	Accurate <i>m/z</i>	t_R (min)	RDB	MS error (ppm)	MS/MS error (ppm)	
P1_Ima			C ₉ H ₉ NO ₄	196.0604	4.5	6	-0.2	15.1 (7)	
P2_Ima			Ima	C ₁₄ H ₁₈ N ₂ O ₃	263.1390	3.4	7	1.1	2.1 (12)
P1_Pro			C ₁₅ H ₂₃ NO ₂ S	282.1522	5.7	5	0.6	5.7 (7)	
P2_Pro			Pro	C ₂₄ H ₃₂ ClNO ₅ S	482.1762	6.0	9	1.1	2.0 (6)
P3_Pro				C ₁₅ H ₂₁ NO ₂ S	280.1366	5.8	6	0.4	3.7 (16)

Table 47. Photodegradation products of Ima e Pro, and their elemental composition, accurate m/z, retention time, number of rings and double bonds (RDBs), mass error, and intensity-weighted average error for the tandem mass spectrometry (MS/MS) data calculated through the number of the product ions reported in parentheses.

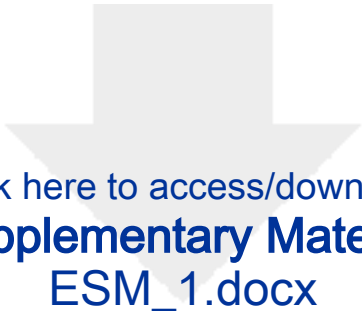
Analyte peak name	Half-life ($t_{1/2}$) (h)	Kinetics constant (k)
Imazamox	1.05	-0.66
Oxadiazon	3.22	-0.21
Profoxydim	5.37	-0.12

Table 58. Half-life and kinetics constants of the three pesticides investigated in paddy water solutions.


Table 9

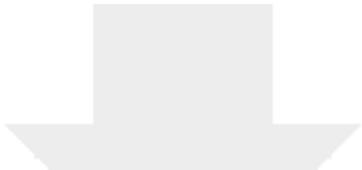
[M+H] ⁺ species	Elemental composition	Accurate <i>m/z</i>	<i>t_R</i> (min)	RDB	MS (ppm)	MS/MS (ppm)
Imazamox	C ₁₅ H ₁₉ N ₃ O ₄	306.1448	3.2	8	-0.1	5.8 (20)
Oxadiazon	C ₁₅ H ₁₈ Cl ₂ N ₂ O ₃	345.0767	6.1	7	0.9	5.1 (6)
Profoxydim	C ₂₄ H ₃₂ ClNO ₄ S	466.1813	5.9	9	0.5	13.5 (25)
Tricyclazole	C ₉ H ₇ N ₃ S	190.0431	3.4	8	-1.1	9.3 (10)
Amidosulfuron	C ₉ H ₁₅ N ₅ O ₇ S ₂	370.0486	4.1	5	0.9	2.7 (12)
DEET	C ₁₂ H ₁₇ NO	192.1379	4.4	5	0.7	15.8 (19)
U2 (P2_Ima)	C ₁₄ H ₁₈ N ₂ O ₃	263.1390	3.4	7	1.1	2.1 (12)
U3	C ₁₄ H ₁₈ N ₂ O ₃	230.1172	3.5	7	0.1	10.3 (27)
U4	C ₁₄ H ₂₅ NO ₄	272.1860	3.7	3	-0.9	14.5 (17)
U5	C ₁₅ H ₂₅ N ₅ O ₃	324.2024	3.6	6	-3.8	19.6 (6)

Table 69: Elemental composition, accurate *m/z*, retention time, number of rings and double bonds (RDB), mass error, and intensity-weighted average error for the tandem mass spectrometry (MS/MS) data calculated through the number of the product ions reported in *parentheses*.




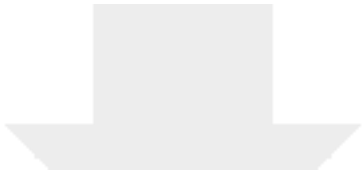
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