

Mitigation of herbicide runoff as an ecosystem service from a constructed surface flow wetland

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Abstract Ecosystem services provided by wetland systems presently play a pivotal role in intensive cropland as water purification from agricultural pollution. A field trial was conducted in 2014 to evaluate herbicide runoff reduction and retention using a 0.32 ha constructed surface flow wetland (CSFW) at the outlet of a 6 ha agricultural basin. To simulate an extreme pulse contamination, the CSFW was flooded with a runoff contaminated with metolachlor, and terbuthylazine and two other subsequent floods with pure water were applied 21 and 65 days later. Results

show that the CSFW can reduce runoff concentration of metolachlor and terbuthylazine by a factor of 45–80 even in extreme flooding conditions. Herbicides retention in the CSFW was reversible, and the second and third floods mobilized 14–31 and 3.5–7.0% respectively, of the amount detected in the first flood. The CSFW performs a high buffer capacity for herbicides, capable to provide water purification service, protecting downstream surface water. Moreover, mitigation capacity of a CSFW for a heavy runoff from a 10 ha basin is 90% for every 50 m in length of a 15 m wide wetland. This confirms that the implementation of CSFWs in agro-systems can improve the sustainability of agricultural production.

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Introduction

The concept of ecosystem services (ES) has recently gained attention both in environmental sciences and practical applications to identify, map and quantify goods and services provided by natural and semi-natural ecosystems to human society (MEA, 2005; Daily & Matson, 2008; Maes et al., 2012). Among these, aquatic and semi-aquatic ecosystems such as wetlands, riparian ecotones and vegetative buffer strips are extremely important in providing, at multiple scales, the full set (provisioning, regulating, supporting and cultural) of ES (De Groot et al., 2006; Power, 2010; Brinson & Eckles, 2011). Particularly, they provide a crucial ES of water purification by pollution control, retention, removal and detoxification of excess nutrients and pesticides (Tanner et al., 2013; Tourné et al., 2013). The water purification service is ensured by complex physical, chemical and biological interaction processes performed within the “plant–soil” system. Moreover, the water purification ES is of paramount importance, particularly in intensive agricultural landscapes that are seriously contributing to non-point source pollution mainly by soil erosion and surface runoff into water bodies, threatening potable water sources, non-target organisms and aquatic ecosystems (Vianello et al., 2005; Lazzaro et al., 2008; Otto et al., 2012). Numerous studies have confirmed that levels of pesticide concentrations in surface waters are undoubtedly linked to crop and soil management practices deployed within the agricultural basins (Dabrowski et al., 2002; Anderson et al., 2011). To reduce the health and environmental risks associated with pesticides, a number of regulations and standards have been implemented world-wide. Recently the EU, in Annex III of Directive 2009/128/EC, issued the thematic strategy on sustainable use of pesticides that highlights the need to implement locally, through National Plans, mitigation actions to protect surface water and non-target organisms (Gregoire et al., 2008; Durel et al., 2015). Therefore, many in-field (e.g. vegetated filter strips, grassed waterways) and off-site (e.g. riparian and artificial wetlands) mitigation systems have been implemented and studied as management practices in crop production, showing significant performances in reducing pesticide loss (Reichenberger et al., 2007; Otto et al., 2012; Vymazal & Brezinová, 2015). Specifically, constructed surface flow wetlands (CSFWs) have been

tested and used extensively in the last decades, showing that they are effective in water pollution mitigation, by retaining sediments and surface runoff; however, efficiency in pesticide control is highly variable according to the physical–chemical properties of the individual pesticide, soil texture and structure, hydraulic retention time and wetland vegetation. It has been found that mitigation effects typically vary from average 35 to 97% (Gregoire et al., 2008; Vymazal & Brezinová, 2015). Trends in removals may be related to chemical groups and even physicochemical parameters of individual pesticides: highest average removals are performed for organochlorine (97%), organophosphate (94%) and pyrethroids (84%); middling values for triazine (63%), chloroacetamide (58%) and triazole (57%). The lowest removal efficiency has been obtained for triazinone (25%) and aryloxyalkanoic acid (35%) (Vymazal & Brezinová, 2015). Kay et al. (2009) reported that for a constructed wetland, the average reduction in pesticide mass loss was 80% and varied from 25 to 100%. In a recent review, Stehle et al. (2011) found that the majority of constructed wetlands retained at least 70% of the entering pesticides, while for Maillard et al. (2011) removal rates varied from 39 to 100%.

Hence, reducing pesticide impacts by implementing off-field CSFWs helps facing the challenge of a better sustainability of crop production in intensive agricultural landscapes.

A field-scale experiment has been ongoing since 2008 on the Experimental Farm of Padova University (north-eastern Italy) to assess the mitigation effect of a CSFW on pollution from agricultural runoff.

The aims of this study were to assess, after a simulated extreme runoff event contaminated with the herbicides metolachlor and terbuthylazine, (1) the mitigation effectiveness of a CSFW in runoff purification, (2) the herbicides and metabolites release after two subsequent controlled floods with pure water.

Materials and methods

Site information and experiment layout

On the Experimental Farm of Padova University, in the Po Valley at North-East of Italy (45°20.951'N 11°57.132'E), a 0.32 ha CSFW vegetated with common reed

(*Phragmites australis*) is located at the outlet of a 6 ha agricultural basin (Maucieri et al., 2014). The CSFW has a discontinuous free flow of water: when runoff occurs from the agricultural basin, a depth of 5–8 cm of runoff flows through the CSFW at about 0.3–0.5 m min⁻¹ from inlet to outlet 200 m apart, coming into contact with plants, litter and soil (Borin & Tocchetto, 2007). In ordinary conditions, only the first 50 m of the CFSW are flooded, the flow is mainly horizontal and residence time is 1–2 h before full infiltration.

Geographical context and experimental design are illustrated in Fig. 1.

In order to fully describe the CSFW and test its hydraulic performance in extreme runoff, a microtopography survey by DGPS and a flood with uncontaminated water had been conducted previously. The CSFW proved to be an enclosed system, without significant drainage.

Therefore, a heavy runoff simulation was performed on 8th April 2014 (first flood), and the CSFW was flooded with 33 m³ of water containing 3800 µg l⁻¹ of S-metolachlor (CAS 87392-12-9) and 2300 µg l⁻¹ of terbuthylazine (CAS 5915-41-3), two of the main herbicides applied to maize to control spring and summer weeds. These concentrations were planned according to the metolachlor/terbuthylazine ratio in ordinary weed control, and were about 1000-fold lower with respect to

an ordinary treatment, and 10,000-fold higher with respect to an ordinary runoff (Cardinali et al., 2013) to simulate an extreme runoff without phytotoxicity but with durable effects. The contaminated flow was followed by another 320 m³ of uncontaminated water applied in 4.5 h in order to flood the whole CSFW under 7–10 cm of water and uniform concentration throughout the 200 m length of the CSFW.

After standardization by the application rate, the calculated water concentrations in the fully flooded CSFW were 2836 µg l⁻¹ kg⁻¹ applied both for metolachlor and terbuthylazine. 15 geo-referenced es of 10 l surface water were then collected proceeding from the CSFW inlet to outlet, a length of about 200 m. Water table samples were also taken. From each 10 l sample, a 1 l sub-sample was taken and placed in an aluminium bottle, sealed and stored in a cooler at +4°C during sampling, then frozen at -20°C until analysis. All water samples were geo-referenced on the field and analysed in GIS environment to perform a spatial correlation analysis.

After 21 days (second flood, 29th April) and 65 days (third flood, 12th June), the flooding was repeated with uncontaminated water, and water samples collected at the same sampling points in order to detect herbicides release according to a sponge-like effect (Otto et al., 2012).

Fig. 1 Constructed surface flow wetland for phytoremediation at the Experimental Farm of University of Padova (Italy): red arrows represent inputs and outputs, white dots the 15 sampling points, blue arrows the water flow path

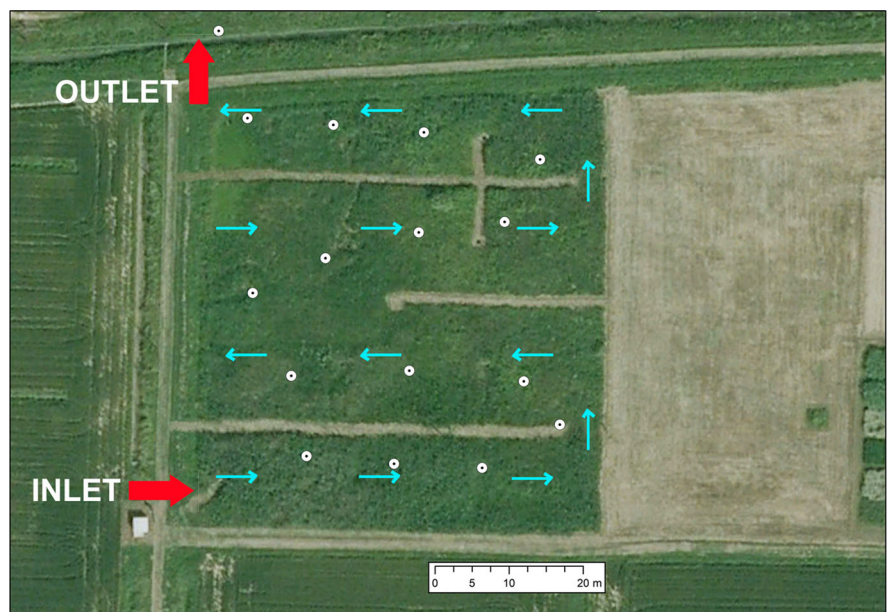


Table 1 Physicochemical properties of the herbicides applied to the CSFW

Parameter (units)	S-Metolachlor	Terbuthylazine	Reference
Appl. rate (kg ha ⁻¹)	1.25	0.75	
CAS	87392-12-9	5915-41-3	MacBean (2012)
Solubility (g l ⁻¹)	0.480	0.009	MacBean (2012)
LogK _{OW}	3.13		Mackay et al. (1997)
		3.04	Di Guardo et al. (1994)
	3.00	3.20	Tomlin (2006)
	3.05	3.40	MacBean (2012)
	3.06	3.21	General mean
K _{OC} (ml g ⁻¹)	121–309	162–378	Tomlin (2006)
	215	270	Tomlin (2006) (mean)
	61–369	162–333	MacBean (2012)
	215	248	MacBean (2012) (mean)
	215	259	General mean
t ₅₀ in field (days)	23	45	Di Guardo et al. (1994)
	14	27	Vianello et al. (2005)
	11–30	30–60	Tomlin (2006)
	21	45	Tomlin (2006) (mean)
	6–49	6.5–149.8	MacBean (2012)
	28	78	MacBean (2012) (mean)
	30	17	MacBean (2012) (median)
	12	20	Otto et al. (2012)
	21	39	General mean

Herbicides physicochemical properties

Metolachlor is about 50-fold more soluble than terbuthylazine (Table 1) according to recent reviews; instead lipophilia (logK_{OW}) is similar or slightly lower for metolachlor.

The adsorption in soil (*K*_{OC}) of metolachlor is also slightly lower (215 vs. 259 ml g⁻¹). Persistence of metolachlor in soil is significantly lower than terbuthylazine in a large selection of soils. Recent studies performed on the Experimental Farm of Padova University (Vianello et al., 2005; Otto et al., 2012) fully confirm this trend, and show that in field conditions of north-eastern Italy, metolachlor is about half as persistent as terbuthylazine, with half-lives of 12–14 and 20–27 days, respectively.

When two chemicals are applied at different rates, a proper comparison of detections is possible taking rate into account. Application rates of metolachlor and terbuthylazine in standard weed control in maize differed, being 1.25 and 0.75 kg ha⁻¹, respectively, so observed concentrations in the CSFW were

standardized by the application rate to ease comparison and better highlight the trend over time, and reported as µg l⁻¹ kg⁻¹ applied.

Analytical procedure

The procedures used derived from previous studies (Dyson et al., 2002; Freitas et al., 2004), were already applied in Otto et al., (2012) and fine-tuned in the present study. Metolachlor (98.0% purity) and terbuthylazine (99.5% purity) standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade methanol and water were used (Fluka). All other chemicals were purchased from Merck (Germany). For all analytes, stock solutions were prepared in methanol (MeOH). The 1 l sample was filtered at room temperature using cellulose nitrate membrane filters of 0.45-µm pore size. After filtration, an acetate buffer solution (2.5 M) was added to the samples in ratio 1% v/v. Samples were cleaned by solid phase extraction using an OASIS[®] HLB sorbent cartridge (60 mg, Waters), earlier conditioned with 2 ml of

MeOH followed by 2 ml of ultrapure water, and a Baker spe-24 G vacuum column processor. Once the samples were extracted, the cartridges were washed with 1 ml of MeOH–water mixture (5:95 v/v) and the excess of water removed by opening the valves of the manifold letting the air to pass through them. The analytes were eluted with 5 ml of MeOH and the aliquots reduced with a gentle nitrogen gas stream at 45°C. The extracts (50 µl) were reconstituted with 1 ml of MeOH.

Metolachlor and terbuthylazine and main metabolites (metolachlor ethanesulfonic acid (Met-ESA), metolachlor oxanilic acid (Met-OA), terbuthylazine-desethyl (TerD), terbuthylazine-2-hydroxy (Ter2H) analyses were performed by LC-MS using a 1100 Series Agilent Technologies system, equipped with binary pump, diode array detector and MSD SL Trap mass spectrometer with ESI source. The optimum values of the ESI-MS parameters were drying gas temperature 350°C; drying gas flow 10 l min⁻¹ and nebulizing gas pressure 45 psi. The detection was carried out considering a mass range of 50–6000 m/z. A Gemini[®] column C18 with TMS endcapping, 150 × 4.6 mm i.d., 3 µm, 110 Å was used to analyse the samples, the mobile phase was composed of water (solvent A) and MeOH (solvent B) both acidified with 0.1% formic acid (60:40).

The LC gradient was isocratic from 0 to 3 min (60% A: 40% B); from 3 to 10 min, a linear increase of B from 40 to 80%; isocratic 80% B from 10 to 13 min; a linear increase of B in 5 min from 80 to 100%. Initial conditions were re-established in 5 min and re-equilibrium time was 5 min.

The flow rate was 0.6 ml/min. A 10 µl sample volume was manually injected each time. Retention times were 11.4 and 10.1 min for metolachlor and terbuthylazine, respectively.

Herbicide concentrations were quantified by comparison with a calibration curve. Individual stock solutions were prepared in methanol/water (60/40, v/v) with concentrations of 100 mg l⁻¹. Mixture solutions were prepared in concentrations of 0.2, 0.5, 1.0 mg l⁻¹. Recoveries of the herbicides from extracted water samples were performed in triplicate at three initial concentrations.

The limit of detection (LOD) and quantification (LOQ) under the chromatographic conditions were determined from the calibration line at low concentrations (Eq. 1):

$$\frac{\text{LOD}}{\text{LOQ}} = \frac{f \times \text{SD}}{b}, \quad (1)$$

where f is factor of 3.3 and 10 for LOD and LOQ, respectively, SD is the standard deviation of the linear regression and b is the slope of the calibration curve. LOQ was 30 ng l⁻¹ for both herbicides. LOD varied between 0.995 and 1.002 ng l⁻¹ for metolachlor and terbuthylazine, respectively.

Runoff mitigation calculation

A clear definition of mitigation for CSFW has not yet been suggested. In this study, the runoff mitigation of the CSFW was calculated taking into account the mass of herbicides in the floods, considering the applied mass as a reference. In general, for two values of mass A and B , with $A > B$, the percentage mitigation from A to B is

$$M\% = 100 \times \frac{A - B}{A}. \quad (2)$$

For example, if in the reference scenario (A) the chemical mass is 5 g, and after complete flooding (B) this amount is 2 g, the mitigation from A to B is $M\% = 100 \times (5 - 2)/5 = 60\%$.

Metabolites occurrence modelling

The aim of modelling of metabolites concentration over time was to outline the occurrence pattern and accumulation risk. When adsorption/desorption of parental and metabolites is not time dependent, then relative abundance is given only to transformation kinetics. Various models for metabolites occurrence are available (Rawlings et al., 1998). When one chemical (M) is being formed by the decay of another (P) at reaction rate A , and is itself decaying at reaction rate B , the simplest model of occurrence of M in time (t) is the two-exponential model (Otto et al., 1997):

$$M = (P_0 - P_0 \times e^{-t \times A}) \times (e^{-t \times B}), \quad (3)$$

where P_0 is the initial amount of P .

Statistical analysis

Correlation between concentrations and distance or duration of flooding was tested with Pearson's r . For Eq. (3), the fit with the experimental data was

evaluated with the coefficient of determination (R^2). All analyses were performed with the software Statistica 10 (StatSoft Inc., 2011).

Results

Concentration after first flood (contaminated runoff)

After complete flooding, as expected, herbicides concentration was almost uniform throughout the CSFW, from inlet to outlet both for metolachlor ($56.3 \pm 35.8 \mu\text{g l}^{-1} \text{kg}^{-1}$) and terbuthylazine ($37.8 \pm 3.77 \mu\text{g l}^{-1} \text{kg}^{-1}$) (mean \pm SD). These values were 45–80-fold lower than the calculated (applied) concentration in the CSFW. The total mass of herbicide detected in the flood was 1.49 g of metolachlor (1.19% of applied) and 1.67 g of terbuthylazine (2.22% of applied). Similar concentrations were found in the water table for both herbicides. Concentrations through the CSFW were independent of distance or flooding time (Fig. 2).

Concentration after second flood

After 21 days, the concentrations in the second flood were lower, both for metolachlor ($8.16 \pm 4.26 \mu\text{g l}^{-1} \text{kg}^{-1}$) and terbuthylazine ($11.8 \pm 11.2 \mu\text{g l}^{-1} \text{kg}^{-1}$) (mean \pm SD). It is worth noting that the second flood mobilized a significant amount of herbicides in about 4.5 h, about 14–31% of the previous one. A correlation with distance and flooding duration was observed for terbuthylazine ($r = -0.653$, $P = 0.041$), likely because in the first part of the flow path in the CSFW, the contact time with the plant–soil complex was double and a greater mobilization occurred. For metolachlor this correlation was not significant, likely its higher solubility and slightly lower lipophilia caused a faster mobilization.

Close to CSFW outlet, concentration of the two herbicides was very similar: 0.59 and $0.37 \mu\text{g l}^{-1} \text{kg}^{-1}$ for metolachlor and terbuthylazine, respectively, values well below the drinking water limit ($0.1 \mu\text{g l}^{-1}$), and the content in the water table was also very low.

Concentration after third flood

After 65 days, the concentrations in the third flood were again very low, both for metolachlor ($0.29 \pm$

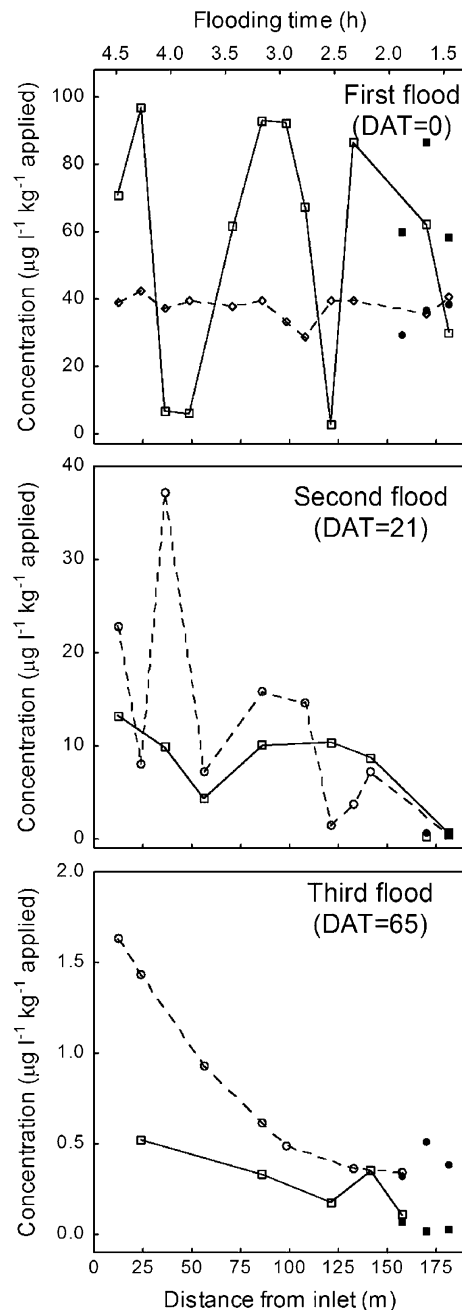


Fig. 2 Concentration of metolachlor (solid line, empty square marker) and terbuthylazine (dotted line, empty circle marker) in the three floods. Full markers are the concentrations in the water table at about 0.6 m depth. All concentrations are standardized by the application rate. The lower axis is the distance from the inlet (m), the upper axis is the time elapsed between flood start and sampling (i.e. the most distant sample was taken last). DAT = days after first treatment. Only samples with detections above the limit of quantification are shown

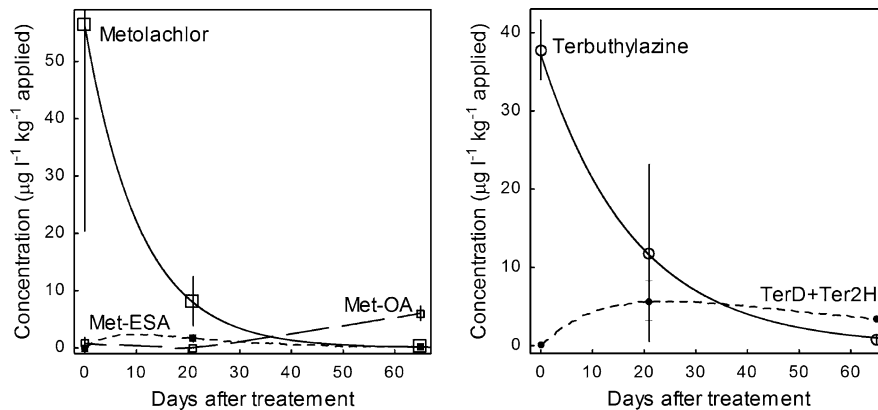


Fig. 3 Herbicides and metabolites concentration in the three floods at 0, 21 and 65 days after treatment (mean + SD) and fitted models (exponential for herbicides, two-exponential for metabolites). Most of the standard deviation bars are lower than the markers. *Met-ESA* metolachlor ethanesulfonic acid; *Met-OA*

metolachlor oxanilic acid; *TerD* terbutylazine-desethyl; *Ter2H* terbutylazine-2-hydroxy. Parameters (st. err.) of Eq. 3 for *TerD* + *Ter2H*: $P_0 = 37.21$, $A = 0.016$ (0.009), $B = 0.030$ (0.008), $R^2 = 0.98$

$0.16 \mu\text{g l}^{-1} \text{kg}^{-1}$) and terbutylazine ($0.82 \pm 0.52 \mu\text{g l}^{-1} \text{kg}^{-1}$) (mean \pm SD), and the amount of herbicides mobilized was about 3.5–7.0% of the previous one. This suggests that reversibility of adsorption lasts for a very long time and is still detectable 2 months after application, even if the amount potentially removable from the CSFW was very low: 0.06 g of metolachlor and 0.5 g of terbutylazine per 1000 g applied to the CSFW. This clearly highlights its mitigation capacity.

As in the second flood, a correlation with distance and flooding duration was observed for terbutylazine ($r = -0.950$, $P = 0.001$) but not for metolachlor.

Close to the outlet, concentration was 0.10 and $0.34 \mu\text{g l}^{-1} \text{kg}^{-1}$ for metolachlor and terbutylazine, respectively.

Mitigation effectiveness

The CSFW was very effective in the reduction (mitigation) of herbicide concentration in runoff. For the first flood, reduction was $(100 - 1.19) = 98.81\%$ for metolachlor and $(100 - 2.22) = 97.78\%$ for terbutylazine. For the second and third flood, average mitigation was about 99.9%.

Metabolites occurrence

The mean concentration of metolachlor and terbutylazine in the three floods was decreasing with time according to an exponential kinetic (Fig. 3), and this is

consistent with known dissipation pattern in soil (Otto et al., 1997).

For metolachlor metabolites, the *Met-ESA* occurrence kinetics was not clear; instead the *Met-OA* was the main metabolite about 30 days after application and with an increasing trend.

The two terbutylazine metabolites show similar trends and were considered together. They occurred with a first-order kinetic and the fitting of Eq. 3 was high ($R^2 = 0.98$). The metabolites concentration overtakes terbutylazine after 35 days; however, the accumulation of metabolites in the CSFW is unlikely, because Eq. 3 predicts a concentration less than $1.0 \mu\text{g l}^{-1} \text{kg}^{-1}$ 130 days after treatment.

Discussion

Under extreme runoff events, the saturation capacity of a CSFW of 3200 m^2 is 353 m^3 , and herbicides concentration is quite uniform in both flowing water and water table. This highlights that in these conditions, the flow in a CSFW is mainly horizontal but also vertical.

Soon after application, mean concentrations of the two herbicides in surface water are similar, according to their similar lipophilia. A certain variability of concentration across the CSFW is likely as roughness and water speed vary along the flow path. The CSFW also has an immediate effectiveness under extreme

runoff events, and reduces the concentration in runoff 45–80-fold, likely because adsorption by the plant–soil complex occurs promptly, in 3–4 h, with a significant reduction of the amount that can by-pass the CSFW and potentially reach surface water. This is fast but, at least for terbutylazine, consistent with other studies conducted with another triazine. Locke et al. (2011) observed a steady decrease in atrazine concentration over a 24-h period, and Hinman & Klaine (1992) observed a rapid plant–soil uptake of atrazine and a fast (2 h) equilibrium between shoots and water.

Adsorption of herbicides is likely superficial and quickly reversed by a subsequent flood. The amount mobilized is low but surface water quality can anyway be affected (Berghahn et al., 2012; Bjergager et al., 2011).

Considering the three floods, concentrations of metolachlor and terbutylazine in the water were very similar and highly correlated ($r = 0.660$, $P < 0.001$). Trend in concentrations standardized by application rate show that terbutylazine overtakes metolachlor 3–4 weeks after application due to its higher persistence.

Metabolites were also detected, showing that degradation is immediate and important and that the flood water from the CSFW contained a mixture of chemicals. Further research could assess accumulation of metabolites and explore the effect of physicochemical properties on adsorption over time.

Field trial results obtained on the Experimental Farm of Padova University show that metolachlor and terbutylazine have a half-life in soil of 11.3 and 19.6 days, respectively (Table 1). This suggests that (1) 3–4 months after application, the residual amount in the CSFW is so low that it makes further mobilization very unlikely even under a heavy flood, (2) there is no risk of accumulation over the years in the CSFW even after repeated spring applications.

In field conditions, metolachlor and terbutylazine are applied with the same timing in spring, mainly to maize. Agricultural runoffs in north-eastern Italian plains are more likely in late spring and early summer (Otto et al., 2012), so the two herbicides are detected in similar concentration. Later events would have a higher terbutylazine content, but this would probably remain unproved because of the scarcity of events and their very low expected concentration.

Conclusions

The CSFW is very effective in the reduction of herbicides runoff even when completely flooded, with a mitigation effectiveness of about 98% for metolachlor and terbutylazine, two of the main herbicides applied to maize. This is in agreement with the conclusions of other recent European studies (Kay et al., 2009; Stehle et al., 2011; Maillard et al., 2011). Comparison with results from other research is possible only after a clear and simple definition of mitigation or removal, as proposed in this study.

It is difficult to single out exactly which processes cause the mitigation. The observed dynamic suggests that in the studied CSFW, the mitigation is provided by a reversible adsorption to the superficial organic matter complex, i.e. by plants, plant residues and soil. In fact, following a successive severe flood, 15–30% of the herbicides detected in the first flood was mobilized after 25, and 40 days later another flood again mobilized a lower but detectable amount of herbicides. In both floods, a mixture of herbicides and metabolites was present. It is worth noting that mobilization of terbutylazine from the CSFW is correlated with the contact time with water, while that of metolachlor, slightly less adsorbed and more soluble, is not. Given that flooding speed is quite regular throughout the CSFW, mitigation can be linked either to the duration or residential time of the flood.

Results highlight that the CSFW is a dynamic system with a high buffer capacity. In ordinary conditions of the plain cropland in north-eastern Italy, where 3–4 runoff events of low volume occur (Cardinali et al., 2013), the mitigation capacity of a 0.3 ha CSFW serving a 6 ha basin is likely complete, i.e. no herbicides will by-pass the CSFW and enter surface water outside the basin.

According to an iterative method for mitigation calculation, hypothesizing a final mitigation of 99.99% for a CSFW of 200 m, the mitigation capacity for a heavy runoff of 3.5 mm from a 10 ha basin is 90% for each 50 m in length for a 15 m wide wetland. This suggests that also smaller CFWS can be very useful at farm scale when other mitigation techniques are implemented, i.e. spray band applications, post-emergence only.

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Compliance with ethical standards

Conflict of interest There is no potential conflicts of interest.

Human animal rights and informed consent This article does not contain any studies with human or animal subjects performed by any of the authors.

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