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Efficient dissipation of acetamiprid, metalaxyl, S-metolachlor and terbuthylazine in a full-scale free water surface constructed wetland in Bologna province, Italy: A kinetic modeling study

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ABSTRACT

The study investigated the dissipation ability of a vegetated free water surface (FWS) constructed wetland (CW) in treating pesticides-contaminated agricultural runoff/drainage water in a rural area belonging to Bologna province (Italy). The experiment simulated a 0.1% pesticide agricultural water runoff/drainage event from a 12.5-ha farm by dissolving acetamiprid, metalaxyl, S-metolachlor, and terbuthylazine in 1000 L of water and pumping it into the CW. Water and sediment samples from the CW were collected for 4 months at different time intervals to determine pesticide concentrations by multiresidue extraction and chromatography-mass spectrometry analyses. In parallel, no active compounds were detected in the CW sediments during the experimental period. Pesticides dissipation in the wetland water compartment was modeled according to best data practices by fitting the data to Single First Order (SFO), First Order Multi-Compartment (FOMC) and Double First Order in Parallel (DFOP) kinetic models. SFO (except for metalaxyl), FOMC and DFOP kinetic models adequately predicted the dissipation for the four investigated molecules, with the DFOP kinetic model that better fitted the observed data. The modeled distribution of each pesticide between biomass and water in the CW highly correlated with environmental indexes as K_{ow} and bioconcentration factor. Computed DT50 by DFOP model were 2.169, 8.019, 1.551 and 2.047 days for acetamiprid, metalaxyl, S-metolachlor, and terbuthylazine, respectively. Although the exact degradation mechanisms of each pesticide require further study, the FWS CW was found to be effective in treating pesticides-contaminated agricultural runoff/drainage water within an acceptable time. Therefore, this technology proved to be a valuable tool for mitigating pesticides runoff occurring after intense rain events.

1. Introduction

Precipitation events in intensively cultivated farmlands produce agricultural runoff which potentially contaminates the surface water network with nutrients and/or xenobiotics. In particular, the contamination of water resources by pesticides was recognized to be a high environmental risk and it is one of the main problems that agricultural sector needs to solve (Meffe and de Bustamante, 2014; Prechsl et al., 2022). In Europe, the use of pesticides is strictly regulated at both national and international level (Directive 2009/128/EC), although the EU is still working on the definition of new best agricultural practices, production protocols and regulations to reduce by 50% the use and risk of chemical pesticides by 2030, in line with the EU's Farm to Fork and Biodiversity strategies. Ground and surface water contamination by pesticides runoff is not an unlikely occurrence (Casado et al., 2019). This phenomenon may be caused by human error, mismanagement, or due to extreme precipitation events which are likely to be more frequent in Mediterranean area and in Italian peninsula in the future (Brunetti et al., 2002; Caporali et al., 2021; Todeschini, 2012).

Constructed wetlands (CWs) are artificial ecosystems that simulate the water treatment processes occurring in wetlands naturally. According to a classification based on water level, CWs can be divided in

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free water surface (FWS) and subsurface flow (SSF) wetlands, which can be further classified into vertical flow (VF) and horizontal flow (HF) (John et al., 2020). These systems are designed and employed to treat water from different sources such as urban/domestic wastewater (Kataki et al., 2021; Wu et al., 2023), stormwater (Livingstone, 1989) or agricultural runoff and/or drainage water (Braschi et al., 2022a; Mancuso et al., 2021; Nan et al., 2023). CWs can remove or degrade a wide range of pollutants (e.g., organic matter, suspended solids, nutrients, pathogens, heavy metals, pharmaceuticals) by the means of physico-chemical processes (e.g., filtration, adsorption, precipitation) and/or biological degradation (Li et al., 2014; Reichenberger et al., 2007; Shilton et al., 2012; Verlicchi and Zambello, 2014; Vymazal, 2013). In addition to the CWs' capacity to dissipate contaminants from polluted water, CWs are also exploited to produce reclaimed water that can be used to irrigate crops (Mancuso et al., 2020, 2022). CWs are also cost-effective and sustainable, with lower operation and maintenance costs compared to conventional treatment systems (Ahmad et al., 2016; Nuamah et al., 2020).

In the rural context, CWs can represent a reliable pollution control solution for preventing the contamination of ground- and surface-water nearby cultivated farmlands due to agricultural water runoff and/or drainage events after pesticides application on crops and/or soil.

CWs capacity to degrade pesticides from agricultural runoff and/or drainage water is rather acknowledged at pilot scale level (Fernández-Pascual et al., 2020; Maillard and Imfeld, 2014; Matamoros et al., 2020; McMaine et al., 2020). In fact, multiple pilot scale studies report enhanced dissipation or degradation for many active principles (Bahi et al., 2023; Imfeld et al., 2021; Stehle et al., 2011).

As an example, a recent study reported triticonazole removal from 49.2 to 88.5% and between 36.6 and 88.4% for the fungicide myclobutanil in a pilot scale horizontal subsurface flow CW (Parlakidis et al., 2023). Another study (Maillard et al., 2016) reported an overall degradation of the herbicide S-metolachlor of 89.7 and 59.5% in batch and continuous flow operation, respectively, in small pilot wetlands with a volume capacity of about 3.5 m^3. A 2011-study reported DT50 varying from 65 to 154 days for the C^{14}-marked fungicide epoxiconazole in incubation experiments mimicking the conditions typical of a CW (Passeport et al., 2011).

However, few studies evaluate pesticides dissipation in full scale wetlands (Maillard et al., 2016), and even fewer propose or discuss kinetic models (Lizotte et al., 2014; Pappalardo et al., 2016). Indeed, most of available dissipation kinetic studies are primarily regulation aimed, so they tend to focus on a single compartment and/or small controlled environments rather than to real scale conditions (AERU, 2023). Nevertheless, larger scale dissipation studies are extremely useful to the scope of risk management of a site, even though such cases are much more complex to model. At real scale, a compound is continuously transferred among compartments via different mechanisms (e.g., volatilization, sorption, desorption, leaching, percolation, runoff, biological uptake) and multiple phenomena contribute to its degradation (e.g., photolysis, hydrolysis, biodegradation). Hence, the kinetic model choice is not trivial and therefore field-scale dissipation studies considering kinetic modeling are scarce. Undoubtedly, more robust data are necessary for establishing or improving risk prediction models which account the role of CWs in the management of contaminated water.

In this work, a simulated runoff/drainage water experiment was conducted on the same FWS CW that had been previously used to investigate its ability for effective pesticide abatement (Braschi et al., 2022a). The present research aimed to further expand the previous studies, using a different set of pesticides, and modeling their distribution in water, based on past experimental observations. With this purpose irrigation water spiked with acetamiprid, metalaxyl, S-metolachlor and terbuthylazine were added to the already half-full FWS CW in late October 2021. Then, during the following days, the system was filled up completely to facilitate pesticide distribution and causing a single controlled outflow for better representing the real FWS CW behavior. No other outflows occurred, and pesticide dissipation within the wetland system (water and sediment) was modeled applying three different kinetic models, so to determine risk management endpoints (DT50 and DT90). Finally, the physical and chemical characteristics of the four active compounds were correlated to some kinetic model coefficients, in the attempt to better elucidate dissipation patterns. The present study on pesticide dissipation kinetics at a field scale adds a solid perspective on the environmental fate of such compounds, as more representative of a stable agricultural ecosystem.

2. Materials and methods

2.1. CW characteristics and hydrology

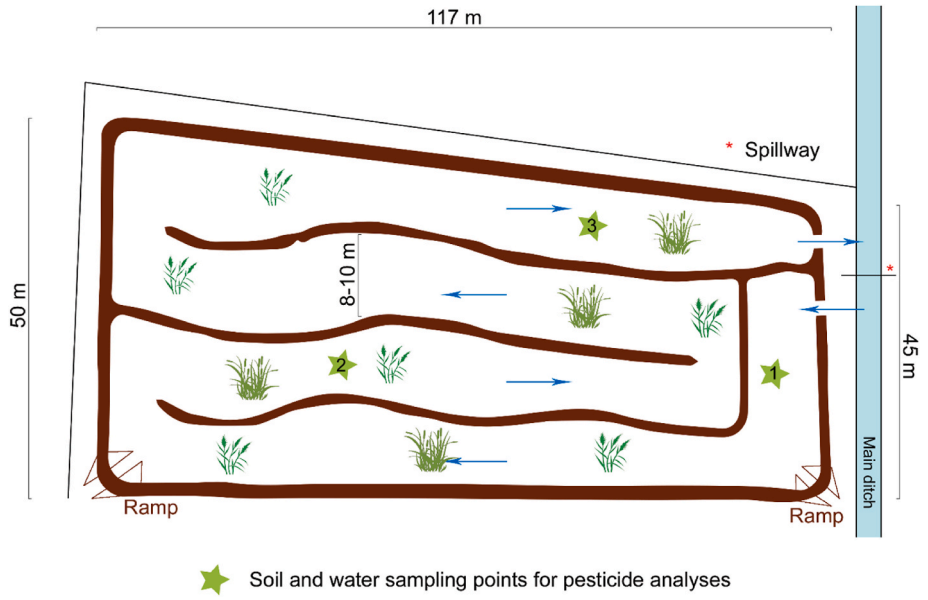
The FWS CW is located at 44°34′21.99″N, 11°31′44.63″E in Budrio municipality of Bologna metropolitan area, within the Emilia-Romagna region, Italy. With a surface of 0.4 ha, it was built in 2000 and operated ever since (Picture 1 A and B). The system was deemed appropriate for the study since it can be considered a mature, semi-natural CW, and therefore can represent relevant environmental conditions at full-scale.

The farmland served by the CW is situated at the Marsili experimental farm of the Canale Emiliano Romagnolo Land Reclamation Consortium, which specializes in horticultural crops and cereals, covering an area of 12.5 ha. The Köppen-Geiger classification categorizes the climate of the site as humid subtropical (Cfa), with an average annual rainfall of 771 mm and most of the precipitation occurring during spring and autumn and a mean annual temperature of 13.7 °C. A meteorological station located within the farm area provides measurements of daily precipitation and average daily temperature.

The entire farmland is drained through a single ditch, from which the runoff and/or drainage water is conveyed to the CW, to be treated before being released into the receiving water ways. Since the farm employs precision irrigation techniques, a consistent amount of water is collected in the ditch only during rainy event causing an excess of water. The CW bed is highly vegetated and hosts indigenous species such as common reed (*Phragmites australis*), cattail (*Typha latifolia*), sedge (*Carex* spp.) and yellow iris (*Iris pseudacorus*). Vegetation occupies about 10% of the CW bed volume (Lavrnić et al., 2020a). Being divided into meanders, the total length of the water flow is approximately 470 m (Scheme 1). The wetland can contain up to 1500 m^3 of water, nevertheless it is normally dry and fills up during intense rain periods only. The water is pumped from the ditch into the CW every time that the water level in the ditch reaches a pre-fixed value (based on the ditch water capacity). The outflow from the FWS CW is triggered by gravity and occurs after the water level inside the system reaches 40 cm. The wetland is equipped with two mechanical flow meters (placed at the entrance and at the exit, respectively) for the measurement of inlet and outlet water volumes and an automatic sensor (located nearby the exit) for the measurement of water level inside the system. Data are recorded hourly and stored by a centralized control unit.

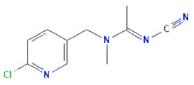
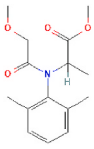
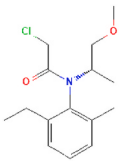
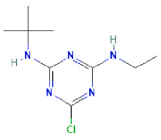
2.2. Plant protection products

Plant protection products used in the study were selected among those in use at the farm. Primagram® Gold (systemic herbicide mixture approved for maize and *Sorghum* crops, concentrated suspension containing 28.9% of S-metolachlor and 17.4% of terbuthylazine) and Ridomil Gold®R WG (water dispersible systemic fungicide for horticultural crops containing 2% of metalaxyl-m) were purchased from Syngenta AG (Switzerland). Epik® SL (liquid suspension for the treatment of multiple crops and fruit trees, containing 4.67% of systemic insecticide acetamiprid) was purchased from Sipcam SPA (Italy). A summary of pesticides' physical and chemical properties is provided in Table 1 (Agriculture & Environment Research Unit AERU, University of Hertfordshire, 2023).



Scheme 1. FWS CW layout. The soil and water sampling points (1, 2, and 3) are indicated by stars.

Table 1
Physical and chemical properties of the active compounds in study. Image source: pubchem.ncbi.nlm.nih.gov, accessed on-line on March 01, 2023.

Structure	acetamiprid	metalaxyl	S-metolachlor	terbuthylazine
				
Molecular weight [g/mol]	222.67	279.33	283.79	229.1
Water solubility [mg L^{-1}]	4250	8400	480	6.6
log K_{ow}	0.80	1.75	3.05	3.40
pK_a	0.7	0	–	2.0
Vapor pressure [mPa]	0.000173	0.75	3.7	0.152
DT50 (water) [days]	4.7	56	9	6
DT50 (water sediments) [days]	NA	56	43.3	70
DT50 (Soil, field) [days]	3	14.1	23.17	21.8
Bioconcentration Factor (BCF) [L kg^{-1}]	<1 on tadpoles (Guo et al., 2022)	7 (whole fish)	68.8 (whole fish)	34 (whole fish)

Aggregated data source: (Agriculture & Environment Research Unit (AERU), 2023) where not differently indicated. NA: Not Available.

2.3. Simulated agricultural water runoff/drainage trial

The experiment was planned to simulate a past real rain event, which generated relevant water runoff and drainage volumes. With this aim, the rain event that has occurred in September 2017 has been selected, during which an overall precipitation of 88 mm (in 20 days) occurred and that has produced a total inflow of around 1900 m^3.

The water used in every stage of the test was drawn from the Canale Emiliano Romagnolo (CER), an irrigation water channel that supplies water to a significant portion of the Emilia Romagna region. The water from the CER ("irrigation water" from now on) is suitable for agricultural use. A full characterization is available as Supporting Table SI1.

On 2021-10-13, 108 g of Primagram® Gold, 625 g of Ridomil Gold®R WG and 250 g of Epik SL (corresponding to 11.68 g of acetamiprid, 12.50 g of metalaxyl, 31.32 g of metolachlor and 18.97 g of terbuthylazine) were dispersed into a tank containing 1000 L of irrigation water and kept under stirring by a submerged mixing pump. The pesticide co-formulants allowed to obtain a homogeneous water suspension. The chosen doses simulated a 0.1% runoff from the entire farm area (12.5 ha) treated with admitted dose of each pesticide.

The pesticides dispersion was then slowly added at the inlet of the FWS CW (near sampling point 1, Scheme 1), which was already filled at half capacity (791 m^3). Irrigation water was pumped intermittently over the next 17 days to simulate the real system behavior during the mentioned event of reference. However, to avoid possible contamination of the surface water network but also to allow effluent sampling, the pumping was planned to produce an outlet of around 50 m^3. Effluent samples were collected and stored at −20 °C until laboratory analyses were performed.

The pesticide Retention Rate (RR) of the FWS CW was calculated using Eq. (1):

$$RR\ [\%] = \frac{V_{in}C_{in} - V_{out}C_{out}}{V_{in}C_{in}} x\ 100 \qquad \text{Eq. 1}$$

where:

V_{out} is the total water volume outflowed from the FWS CW in L.

C_{out} is the active compound concentration of the outflowed volume in mg L^{-1}.

V_{in} is the total water volume pumped into the FWS CW in L.

C_{in} is the active compound concentration in input water mg L^{-1}.

2.4. Sediment and water sampling

Water and sediment samples within the FWS CW were collected starting from 2021-10-15 and after 5, 12, 19, 26, 56, 88 and 118 days. The two-days latency period between spiking and first sampling was chosen according to fluid dynamics observations from previous works on the same FWS CW (Braschi et al., 2022b; Lavrnić et al., 2018), and was purposely chosen to let pesticides distribute more uniformly along the FWS CW.

On each sampling day, three sediment and three water samples were collected at points 1–3 shown in Scheme 1. Water samples were collected using a bailer sampler (Geotech environmental equipment Inc., Colorado, USA) and placed in a 1 L polypropylene bottle. Three core sediment samples were collected at each sampling point using a root auger (Eijkelkamp), paying attention to avoid repeated sediment sampling of the exact same spot. Plastic markers were used to this purpose. Core samples, 30 cm long, were divided into four distinct portions: from 0 to 5 cm, 5–10 cm, 10–15 cm, and 15–30 cm deep lastly. Single portions were cleansed from vegetal debris. Finally, within each sampling point, sediment of the same depth was pulled together and homogenized. In the end, on each sampling date twelve homogenized sediment samples (four depths x three points) and three water column sample (1 L x three points) were collected. Water and sediment samples were immediately stored at −20 °C until analysis.

2.5. Pesticide multiresidue analyses

Pesticides residues analyses of water and sediment samples were commissioned to external certified laboratory Tentamus Agriparadigma S.R.L. (Accredia registry 0060 L, Ravenna, Italy).

Pesticide residues analyses of water and sediment samples were extracted through method 5060 and 5100 by Italian Environmental Protection and Technical Services Agency (APAT) (APAT & CNR-IRSA, 2003). Briefly, 100 mL of water sample were added with an internal standard and extracted three times with dichloromethane. Extracts were evaporated through a Rotavapor (Büchi Labortechnik AG, Switzerland) up to 5 mL and transferred in graduated vial where a light nitrogen flow completely evaporated the dichloromethane extracts. Either 1 mL of ethyl acetate or methanol (both MS grade) were added to the dry extracts, rinsing repeatedly the vials. Both extracts were finally transferred in chromatographic vials for analysis.

Sediment samples were extracted by Italian National Standard Body (UNI) method 15662:2018 (UNI EN, 2018). Briefly, 10 g of sediment sample were added with an internal standard, extracted with 10 mL acetonitrile, vigorously shaken on a vortex for 60 s, added with 4 g $MgSO_4$, 1 g NaCl, 0.5 g disodium hydrogen citrate sesquihydrate, centrifuged at 4478 *g* for 5 min then refrigerated at −20 °C for 24 h. Extracts were further purified by adding 150 mg Primary Secondary Amine (PSA) sorbent and 900 mg $MgSO_4$, stirring for 30 s and centrifuging at 4478 *g* for 5 min. Such extracts were split into 2 aliquots: 1) half the extract was diluted with MS-grade water and transferred into chromatographic vials for LC, while 2) the remaining half was dried under light nitrogen gas flow and added with a 1:1 ethyl-acetate/cyclohexane solvent mixture, then transferred into GC vials.

The LC-MS/MS system was composed by an Acquity Ultra High-Performance Liquid Chromatograph (UPLC) and a Xevo TQ-S mass spectrometer by Waters (US). The GC system consisted in a 7010 B triple quadrupole integrated GC by Agilent (US).

The analytical measurement error for acetamiprid and metalaxyl was ±30% while it was ±40% for metolachlor and terbuthylazine.

2.6. Kinetic modeling data handling and analysis

Data quality assurance was conducted according to best practices indicated by European Food Safety Authority (EFSA) guidance document (EFSA, 2014). Raw pesticide concentration in water below the limit of quantitation (LOQ) were set to ½ LOQ. Data from the three sampling points was averaged and multiplied by the CW water volume, obtaining pesticide total mass within CW water. Data fitting, parameter optimization and endpoints calculation was performed in R environment (R version 4.1.3.) using mkin package (version 1.2.2.) (Ranke, 2022).

2.7. Model assumptions and selection

Two main assumptions were made: (i) according to the low vapor pressure of the pesticides under study (<4 mPa, see Table 1), their transfer to atmosphere by volatilization from the water compartment was deemed negligible, and (ii) the photolysis was considered negligible as well because of the wide development of plant biomass covering the water surface (see Picture 1B).

To ensure physical dispersion of pesticide formulations, two days elapsed between spiking of the FWS CW and the first measured data point. Theoretical initial concentration was not considered in modeling: rather, only measured concentrations were used (from 2021-10-15 onward). Metabolites were not considered in the dissipation models as their study was beyond the scope of the present work. Water column was selected as output compartment. Applied kinetic models were: Single First Order (SFO), First Order Multi-Compartment (FOMC), and Double First Order in Parallel (DFOP).

Each kinetic model is described as an exponential equation in which the mass (P) of a chemical after a given time (t) is a function of the initial mass (P_0). Model coefficients (parameters) and formulas differ in each kinetic model. Briefly, SFO is described by Eq. (2):

$$P = P_0 e^{-kt} \quad \text{Eq. 2}$$

where *k* is the dissipation rate over time.

FOMC is a stochastic model, described by Eq. (3):

$$P = P_0 \left(\frac{t}{\beta} + 1\right)^{-\alpha} \quad \text{Eq. 3}$$

where α and β are parameters of the underlying probability density function Γ (Gustafson and Holden, 1990).

Finally, DFOP model (Eq. (4)) assumes two distinct dissipation rates (k_1 and k_2) within two separate compartments in which the whole pesticide mass is partitioned by the quotas "*g*" and "1-*g*".

$$P = P_0 \left(g e^{-k_1 t} + (1 - g) e^{-k_2 t}\right) \quad \text{Eq. 4}$$

3. Results and discussion

3.1. Free water surface constructed wetland hydrology

The hydrology of the system during the experimental period (from 2021-10-13 to 2022-02-10) is given in Fig. 1. Most of the inflow (red line) was due to pumping of irrigation water into the wetland. Only a small part (4.3%) of the inflow to the system was a result of direct precipitation over the wetland surface (green line). Observed hydrology data are in accordance with data reported in the literature, where direct precipitation usually contributes for a smaller portion of the water entering a CW, compared to other sources such as surface runoff, groundwater flow, or intentional water input from sources such as stormwater drains or sewage systems (Jiang and Chui, 2022; Lavrnić et al., 2020b). The significance of direct precipitation can vary based on location, climate, and the design of the CW (Stefanakis, 2020).

As previously said, the outlet from the system is present only when the water level is above 40 cm, a condition that was fulfilled only on 2021-10-27, when 55 m^3 of water exited the FWS CW outlet. After that, the inlet pumping has continued for 2 more days to maintain the constant water level in the system, avoiding any further outflow.

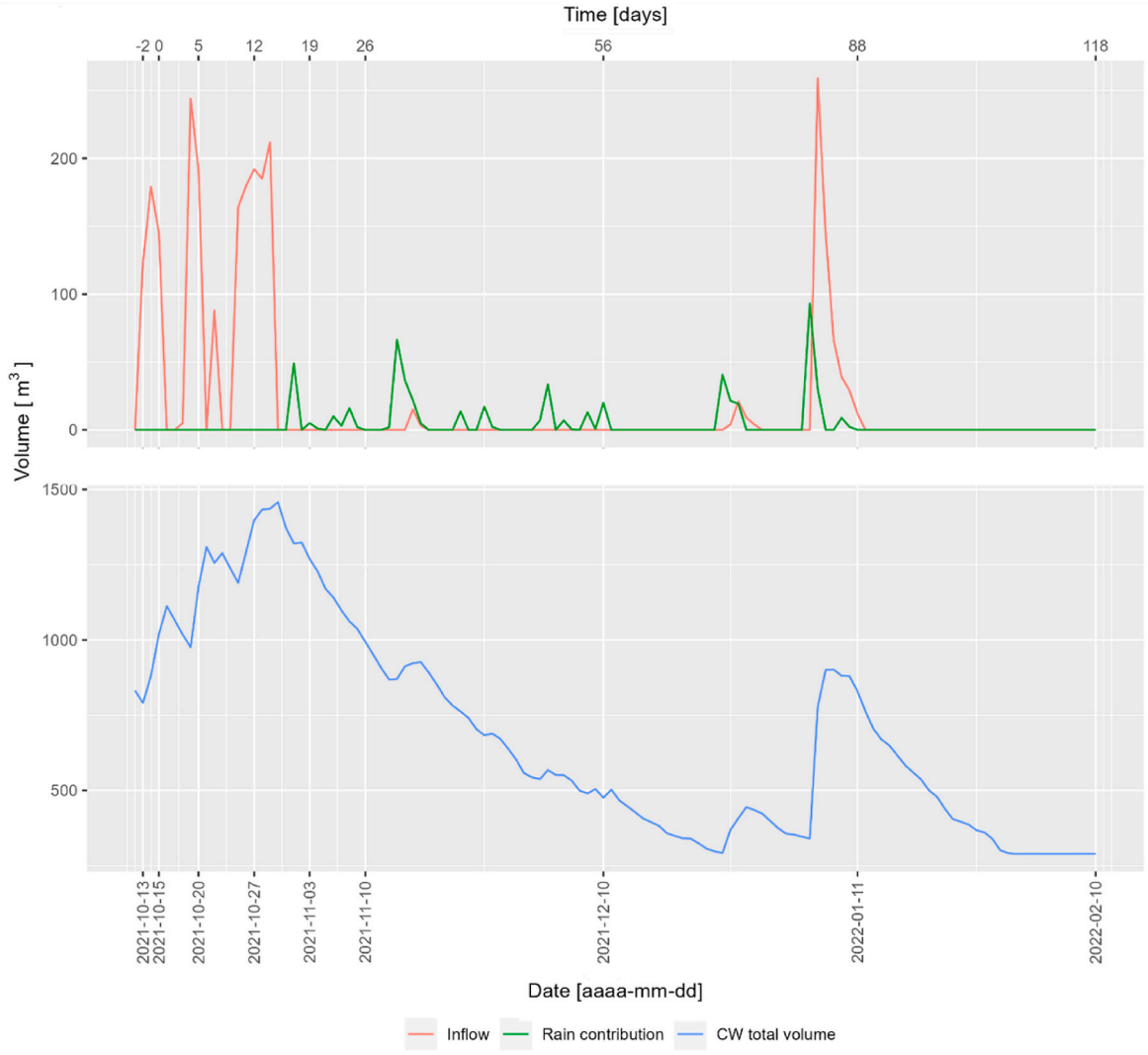


Fig. 1. CW hydrology during the trial. X scale breaks correspond to trial beginning (2021-10-13) and sampling days starting from 2021-10–15 (days 0, 5, 12, 19, 26, 56, 88, and 118, respectively).

3.2. Pesticide retention by the CW

The water that outflowed from the FWS CW on 2021-10-27 (55 m^3), contained pesticide traces as reported in Table 2. The calculated RR (see Eq. (1)) were 99.937, 98.952, 99.953 and 99.968% for acetamiprid, metalaxyl, metolachlor and terbuthylazine, respectively. Thus, the CW retained most of the pesticides mass (≥99.937%, on average). The outflow of pesticide mass was small enough to be considered negligible in comparison to the mass contained into the CW, thus allowing to model the pesticide dissipation within the wetland (vide infra).

Table 2
Pesticides output after two weeks from spiking and retention rates.

	Acetamiprid	Metalaxyl	S-Metolachlor	Terbuthylazine
Input theoretical spike ($V_{in}C_{in}$) [mg]	11,675	12,500	31,320	18,972
Outflowed water concentration (C_{out}) [μg/L]	0.15	2.14	0.27	0.09
Outflowed water volume (V_{out} on day 12) [L]	55,000	55,000	55,000	55,000
Output pesticide quantity ($V_{out}C_{out}$) [mg]	8.25	117.7	14.85	4.95
Retention rate (RR) [%]	99.937	98.952	99.953	99.968

3.3. Pesticide concentration in sediments and water column

All multiresidue analyses performed on the sediment samples resulted to be below LOQ for the four considered compounds at every sampling point and at any time. Despite the molecules' pK_{ow} higher than 1 (acetamiprid excluded, see Table 1), that is generally considered an index of hydrophobicity, no detectable traces of pesticides were found in the sediment core samples. Reasonably, the heterogeneous and thick organic substrate, made of mucilaginous biofilms, algae, and plant debris, developed at the FWS CW bottom, prevented the water-dispersed pesticides to be sorbed into the sediment (Kurzbaum, 2022).

Punctual water column concentration of active compounds in the three sampling points is reported as supporting information in Figure SI1. The punctual concentrations (points 1–3) were averaged by day, then multiplied by daily water volume, to account for water volume

variation. Finally, resulting pesticides mass data are shown in Table 3.

Here, each pesticides' first mean observed quantity in water (sampled on 2021-10-15, two days after spiking) revealed to be rather similar to the theoretical quantity used for spiking, meaning that little to no dissipation occurred in the 2 days elapsed. On the following sampling days, pesticide mass within water column decreases progressively. Apart from metalaxyl, more than 90% of pesticide mass dissipated before the complete filling of the CW (see 2021-10-27 data point, Table 3). Surprisingly, pesticides measured amounts on the subsequent data point (19th day, 2021-11-3) was higher than the previous ones. This data anomaly may be due to an alteration of water flow within the CW after the controlled outflow, or due to sheer chance. Since the data heterogeneity was still compatible to analytical errors of pesticides quantitation, the data point was not discarded.

The dissipation rate of pesticides in CWs can vary significantly based on various factors such as the type of pesticide, its chemical properties, the system design, environmental conditions, and microbial activity within the wetland (Liu et al., 2019). Some pesticides may degrade relatively quickly due to exposure to sunlight, microbial degradation, or chemical reactions in the water and soil, while others might persist for longer periods. Typically, studies have shown that the pesticide dissipation half-life (the time taken for half of the initial concentration to degrade) in CWs can range from a few days to several weeks or even months (Gilevska et al., 2023). In this study, confirming the high CW efficiency, a rapid mass reduction for all the four investigated pesticides was detected within five days from the initial sampling, ranging from 79% for metalaxyl to 89% for S-metolachlor. In the study of Jing et al. (2021), the influence of different CW substrates (e.g., superabsorbent polymers and gravel) on metalaxyl dissipation was examined. CWs with superabsorbent polymers dissipated 50–84% of metalaxyl, while those with gravel substrates retained 32–97% over 44 days, considered the required duration for stable CW operation. Lower S-metolachlor dissipation rates were observed by Zheng et al. (2022), with the highest reduction of about 39% detected within the first 40 days of the experiment, while the relative magnitudes of the dissipation dropped down after 40 days. The mature full scale FWS CW that was examined in our study showed better performance, dissipating 95.6% of acetamiprid, 89.5% of metalaxyl, 98.3% of S-metolachlor and 97.8% of terbuthylazine initial theoretical quantities in 12 days, before filling up the system completely. Very low residual concentrations in the water column were detected at the end of the observing period (118 day since initial sampling), proving that all the pesticides were nearly entirely eliminated.

3.4. Kinetic models and visual fitting

The absence of dissipation within the 2 days following the spiking discussed above could have been interpreted as a lag-phase or logistic dissipation kinetics and modeled accordingly, so that the theoretical point would have been accounted as "true" starting point. However, the model was not considered for the following reasons here described. No clear evidence of lag-phase kinetics was found in literature for the considered compounds. Only in a 2002 paper about 30 days of lag phase were reported for S-metalaxyl, a stereoisomer different from that used in our study and that is biologically inactive and non-present in modern formulations (Buser et al., 2002). Moreover, in our study, the possible lag phase was similar for all the four compounds, after that the dissipation started abruptly. Therefore the 2 days apparent "lag phase" was more reasonably considered as an experimental artefact due to the incorporation in co-formulants and emulsifiers of the active ingredients, whose release into the water column took about two days after their introduction into the FWS CW. Consequently, the logistic kinetic model was ruled out from this study and only observed data points were considered for fitting.

The zero-order kinetic model was ruled out as well, because of the steepness of the data point curve. Finally, the hockey-stick kinetic model was not considered because of the absence of a clear dissipation rate discontinuity at a precise time.

The three kinetic models that were deemed appropriate to be used in this study were SFO, FOMC and DFOP. The choice was motivated by the following evidence.

1. SFO dissipation kinetics is descriptive of the dissipation of several compounds of environmental concern as pesticides in different compartments as water or soil. Its easy application makes this kinetic model highly adopted in the literature in that the DT50 of a given species is independent from the initial concentration (DT50 = ln2/k);
2. FOMC dissipation kinetics was considered plausible since, in a large and heterogeneous environmental system as CWs, dissipation rates could follow a distribution rather than a single and uniform rate;
3. DFOP dissipation kinetic accounts for molecules partition between two sub-compartments (e.g., in the wetland, between water and another compartment as soil, or microbial biomass, or plants), in which dissipation occurs with two distinct degradation rates. Since the studied vegetated CW had at least two sub-compartments (water column and organic biomass), the kinetic model was considered in this study.

For each pesticide, the mean observed quantity at a given day was transformed into percentage value with respect to the first observed amount (100%) and fitted to SFO, FOMC and DFOP kinetic models. Fig. 2 illustrates the fittings of observed quantities of acetamiprid, metalaxyl, metolachlor and terbuthylazine to the three selected models (Fig. 2, graphs A-1, B-1, C-1 and D-1), along with residuals diagram (Fig. 2, graphs A-2, B-2, C-2 and D-2).

In Fig. 2, optimized kinetic models for SFO, FOMC and DFOP are plotted on the left panels, while the right panels show their residuals. By visual assessment, the goodness of fit seems to be DFOP > FOMC > SFO for all four compounds. The compound with the worst fitting is metalaxyl, especially with SFO model.

Not surprisingly, SFO had the worst fitting. This kinetic model adequately predict dissipation when their rate is constant, which usually occurs when it is due to a distinct mechanism (e.g., hydrolysis, biodegradation) (Torabi et al., 2017, 2022) in a homogeneous medium, but fails to be accurate when these conditions are not met. Such is the case of the full-scale wetland considered in this study, which is spatially heterogeneous and may employ several different degradation/dissipation/transfer mechanisms.

Considering the underlying assumptions of FOMC and DFOP, the better fitting of DFOP with respect to FMOC may suggest that dissipation is better described by the occurrence of two discrete mechanisms in distinct environmental sub-compartments, rather than the presence of a single phenomenon with stochastically distributed rates (Gustafson and Holden, 1990; Sarmah and Close, 2009).

Table 3
Active compound mass dissolved in wetland water column.

	Pesticide mass in the water column [g]			
	Acetamiprid	Metalaxyl	S-Metolachlor	Terbuthylazine
Theoretical spike at date				
2021-10-13	11.68	12.50	31.32	18.97
Observed quantity at date (days since initial sampling)				
2021-10-15 (0)	13.04	11.23	31.78	15.32
2021-10-20 (5)	2.071	2.350	3.387	2.522
2021-10-27 (12)	0.509	1.308	0.518	0.417
2021-11-3 (19)	1.134	1.936	0.772	0.477
2021-11-10 (26)	0.711	1.271	1.315	1.148
2021-12-10 (56)	0.185	0.216	0.203	0.147
2022-01-11 (88)	0.138	0.067	0.081	0.070
2022-02-10 (118)	0.058	0.011	0.021	0.035

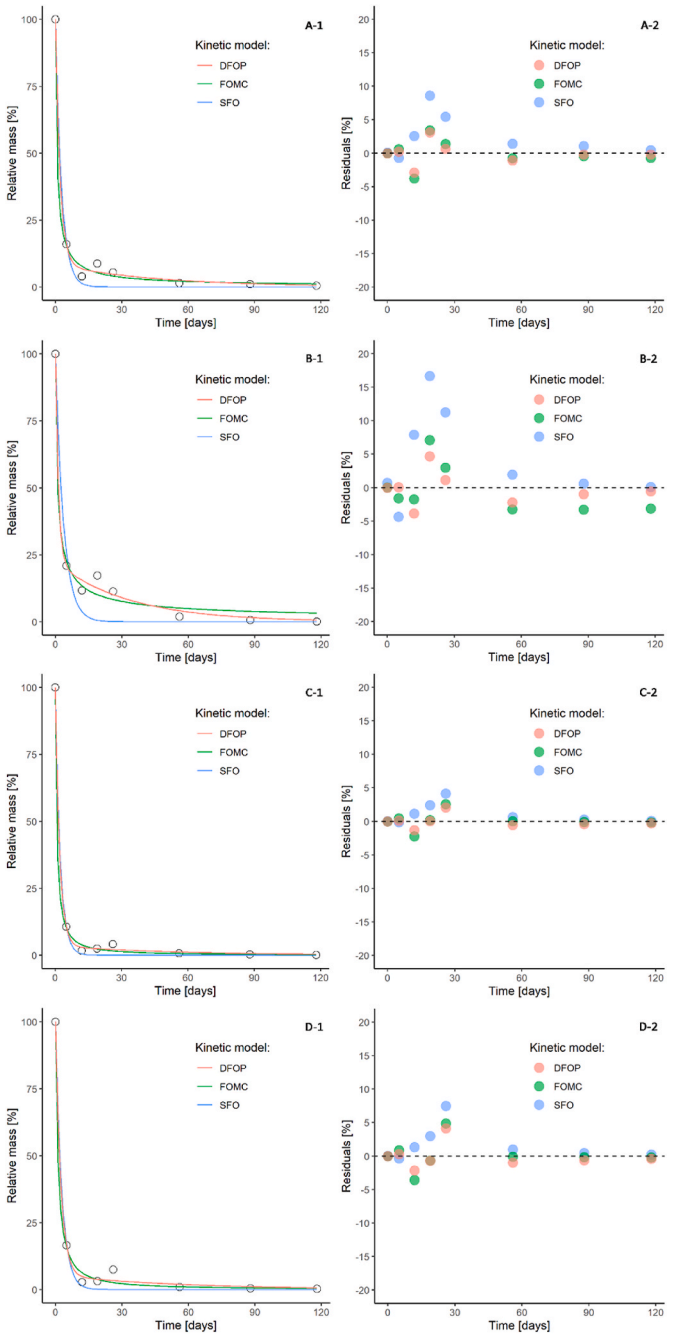


Fig. 2. Acetamiprid (A), metalaxyl (B), S-metolachlor (C) and terbuthylazine (D) plots of dissipation with fitted models (1) and corresponding residuals plot (2).

3.5. Model endpoints and goodness of fit

In Table 4 are reported the summary statistics of the three models for the chosen molecules, that is, optimized parameters, χ^2 statistics and DT50 and DT90 as selected model endpoints.

The three investigated kinetic models gave acceptable fitting for the dissipation of acetamiprid. Nevertheless, according to the χ^2 statistics (Table 4), the goodness of fit was in the order: DFOP (model $\chi^2 = 0.745$) > FOMC (1.118) > SFO (4.321). The metalaxyl dissipation data rejected the SFO model as model χ^2 (13.02) was higher than tabulated χ^2 (12.59) and, consequently, the χ^2 minimum error (30.51) was higher than the analytical measurement error (30%). On the contrary, both FMOC and DFOP models fitted the dissipation with a goodness in the order: DFOP (model $\chi^2 = 1.172$) > FOMC (2.552). As far as metolachlor was concerned, its dissipation kinetics fitted the three models with a goodness of fit in the order: DFOP (model $\chi^2 = 0.556$) > FOMC (0.876) > SFO (1.577). Likely acetamiprid and metolachlor, also the fitting goodness for the dissipation kinetics of terbuthylazine followed the order: DFOP (model $\chi^2 = 0.556$) > FMOC (0.876) > SFO (1.577).

In agreement with visual assessment of data (Fig. 2), χ^2 statistics resulted in an excellent fitting to DFOP model, good fitting to FOMC, and adequate fitting to SFO for all pesticide in this study (except for metalaxyl, for which SFO was rejected). To note, all FOMC and DFOP DT50 values were calculated as DT90/3.32, as prescribed by guidance lines (EFSA, 2014), since more than 90% of dissipation occurred within the study period and models were acceptable.

By comparing the DT50 calculated by the acceptable models, similar values were found for acetamiprid (1.931, 2.169 and 2.606 d for SFO, DFOP and FOMC, respectively), metolachlor (1.533, 1.551 and 1.557 d for FOMC, DFOP and SFO, respectively), and terbuthylazine (1.945, 2.047 and 2.346 for SFO, DFOP and FOMC, respectively), meaning that these models were quite equivalent in predicting the half-life time of the pesticides in the FWS CW. All these molecules halved in about 2 days. On the contrary, metalaxyl DT50 values of accepted models (FOMC and DFOP) were longer, and quite diverse (5.836 and 8.019 d, respectively). In all cases, all the four pesticides' DT50 were shorter than the tabulated DT50 in water (4.7–56 d, Table 1), thus indicating the positive effect of the biological activity within the FWS CW.

Any comparison between DT50 of a pesticide obtained by different studies in different conditions must be taken with caution. Design, location, scale, maturity, and composition of vegetated CW vary significantly and there are no sufficient data in literature to allow reliable comparison. Table 1 reports the pesticides' tabulated DT50 obtained in standardized study. In water, metalaxyl DT50 (56 d) > S-metolachlor (9 d) > terbuthylazine (6 d) > acetamiprid (4.7 d). With respect to tabulated DT50, dissipation obtained in the CW reduced significantly in an almost proportional manner. Table 5 shows a brief selection of research papers in which CW systems were employed to treat any of the considered pesticide. Pappalardo et al. (2016) studied a full-scale vegetated CW but focused on soil, obtaining a DT50 of 11.3 days for S-metolachlor and 19.6 days for terbuthylazine. In a 2011 study, Maillard (Maillard et al., 2011) examined a full-scale system as well, but did not follow a kinetic modeling approach and thus no DT50 was calculated. In some cases, Lizotte obtained DT50 as short as that in our study for S-metolachlor, in a 2014 paper (Lizotte et al., 2014). As stated in the introduction, pesticides dissipation studies on full scale CW system are scarce and often do not involve kinetic modeling.

From an environmental point of view, since the FWS CW is expected to abate the pollution of collected water and to return it with ameliorated quality, the most relevant endpoint to the scope of risk management is DT90, when 90% of the compound is removed. Again, the ranges of DT90 calculated by the three dissipation models for acetamiprid (between 6.416 and 8.657 d), metolachlor (5.094–5.173 d), and terbuthylazine (6.462–7.794 d) were found very narrow. Metalaxyl DT90, on the contrary, ranged from 19.39 (FOMC model) to 26.64 days (DFOP model). Coherently, its optimized dissipation curve and corresponding percentage of residuals (Fig. 2) varied significantly by adopting the two models. From a practical point of view, since more than one model had acceptable fit for each molecule, good practice prescribes to adopt the highest dissipation endpoint as a precautionary measure, to the context of farmland management.

As the FWS CW filled on 2021-10-27, 55 m^3 of water outflowed from the system. On that occasion, most of pesticide mass was already dissipated, according to our models. Not surprisingly, only 8.25, 117.7, 14.85 and 4.95 mg of acetamiprid, metalaxyl, metolachlor and terbuthylazine exited the FWS CW, respectively. This corresponded to a spill out of 1.62, 9.0, 2.9 and 1.2% of their total mass within the CW on the same day, respectively. The effect of the outlet was considered negligible with respect to modeling, since the "spilled out" mass was, in percentage

Table 4
Theoretical and observed mean concentration of the pesticides in the wetland water column over time and dissipation models summary of statistics. Model is rejected (figures in red) if Model χ^2> Tabulated χ^2, or χ^2 minimum error > analytical measurement error. DF = Degrees of Freedom. DT50 marked with * were back calculated from whole model's DT90 (DT50 = DT90/3.32).

	Acetamiprid	Metalaxyl	S-Metolachlor	Terbuthylazine
Theoretical and observed concentration				
Initial mean theoretical quantity [mg]	11675	12500	31320	18972
Initial mean observed quantity [mg]	13039	11231	31784	15317
Relative mean observed quantity at:				
t = 0 days [%]	100	100	100	100
t = 5 days [%]	15.88	20.92	10.66	16.46
t = 12 days [%]	3.902	11.64	1.631	2.721
t = 19 days [%]	8.700	17.23	2.428	3.111
t = 26 days [%]	5.451	11.32	4.137	7.494
t = 56 days [%]	1.420	1.925	0.639	0.963
t = 88 days [%]	1.055	0.600	0.255	0.458
t = 118 days [%]	0.441	0.095	0.065	0.231
Analytical measurement error [%]	30	30	40	40
SFO kinetic model				
Optimized parameters:				
P_0	99.92	99.29	99.99	99.96
k [$days^{-1}$]	0.359	0.273	0.445	0.356
χ^2 statistics				
Model χ^2	4.321	13.02	0.689	1.577
Tabulated χ^2 (5%, DF = 6)	12.59	12.59	12.59	12.59
χ^2 minimum error [%]	17.57	30.51	9.356	14.15
Endpoints:				
DT50 [days]	1.931	2.535	1.557	1.945
DT90 [days]	6.416	8.419	5.173	6.462
FOMC kinetic model				
Optimized parameters:				
P_0	100.0	99.98	100.0	100.0
α	0.846	0.634	1.241	1.226
β [days]	0.610	0.526	0.944	1.408
χ^2 statistics				
Model χ^2	1.118	2.552	0.334	0.876
Tabulated χ^2 (5%, DF = 5)	11.070	11.070	11.070	11.070
χ^2 minimum error [%]	9.532	14.40	6.943	11.25
Endpoints:				
DT50 [days]	2.606*	5.836*	1.533*	2.346*
DT90 [days]	8.657	19.39	5.094	7.794
DFOP kinetic model				
Optimized parameters:				
P_0	100.0	100.0	102.9	100.0
k_1 [$days^{-1}$]	0.486	0.757	0.626	0.425
k_2 [$days^{-1}$]	0.217	0.030	0.098	0.018
g	0.915	0.778	0.987	0.946
χ^2 statistics				
Model χ^2	0.745	1.172	0.179	0.556
Tabulated χ^2 (5%, DF = 4)	9.488	9.488	9.488	9.488
χ^2 minimum error [%]	8.405	10.54	5.496	9.68
Endpoints:				
DT50 [days]	2.169*	8.019*	1.551*	2.047*
DT90 [days]	7.206	26.64	5.153	6.799

much lower than the analytical error (30–40%) incorporated in the model.

In accordance with visual assessment, FOMC model fitted better than SFO for our substances. FOMC model by Gustafson & Holden accounts for this variability by assuming that a natural compartment may be spatially divided in multiple sub-compartments, each of them with its own first-order dissipation rate. Dissipation rates of the "n" compartments are stochastically distributed according to the Γ distribution,

Table 5
Selected research on acetamiprid, metalaxyl, S-metolachlor and terbuthylazine dissipation in full scale or pilot CW.

Pesticide	Dissipation rates	DT50	CW feature	Source
S-metolachlor	89.7% water load reduction over 77 days in batch experiments		Small controlled environment pilots	Maillard et al. (2016)
S-metolachlor		16–276 h (water)	Large vegetated mesocosm	Lizotte et al. (2014)
terbuthylazine		30 days (water)	Small controlled environment pilots with Typha latifolia	Papadopoulos and Zalidis (2019)
terbuthylazine		8.1 days (water)	Small controlled environment pilots	Gikas et al. (2018)
S-metolachlor		11.3 (soil)	Surface flow vegetated full-scale CW	Pappalardo et al. (2016)
terbuthylazine		19.6 (soil)	Surface flow vegetated full-scale CW	Pappalardo et al. (2016)
metalaxyl	70% water load reduction over 176 days in batch experiments		Full-scale stormwater CW	Maillard et al. (2011)
terbuthylazine	100% water load reduction over 176 days in batch experiments		Full-scale stormwater CW	Maillard et al. (2011)
acetamiprid	not detected	–	Microcosm	Gorito et al. (2018)

whose density function is described by α and β parameters. Small α and β (<1) describe a heavily right-skewed distribution (Gustafson and Holden, 1990). In the case of metalaxyl, the model tends to overestimate the concentrations past the 50th day, suggesting that the Γ distribution may not represent well the actual one.

DFOP model assumes that the dissipation within a system may be factored into two main compartments in which the entire pesticide mass is partitioned, so that the output mass compounds two different degradation rates, occurring simultaneously. The best general fitting of our pesticides to DFOP kinetics suggests that this is the most appropriate model to predict the degradation of the pesticides considered, in our wetland. Moreover, the relatively small residuals on later days indicate a very good accuracy in predicting long-term dissipation. For these reasons, it may be inferred that this model assumptions better describe the FWS CW with respect to the others.

In detail, DFOP parameters meaning can be read as follows: after inserting a M_0 mass in a system, over time a fraction "*g*" of said mass ends up in compartment 1, which degrades the mass at the faster rate k_1, while a fraction equal to "(*1-g*)" ends up in the second compartment, degrading at the slower rate k_2. To note that while k_1 is always higher than k_2, as the first is always the faster, this is not necessarily true for *g* and (*g*-1), which are arbitrarily chosen upon their degradation rate. In our experiment, the mass quota of acetamiprid, metolachlor and terbuthylazine in the fastest degrading sub-compartment *g* was consistently high (91.5–98.7%, Table 4) with daily dissipation rates ranging between 42.5 and 62.6%. The remaining quota (8.5–1.3%) occurring in the lowest degrading compartment showed a daily dissipation rate of 1.8–21.7%. Metalaxyl had the lowest compartment mass ratio (Table 4), meaning that hypothetically only 77.8% of its mass was confined in the quickest degrading compartment (dissipation rate $k_1 = 75.7\%$) while the remaining 22.2% transfers to the lowest dissipating compartment where it degrades at $k_2 = 3\%$ rate.

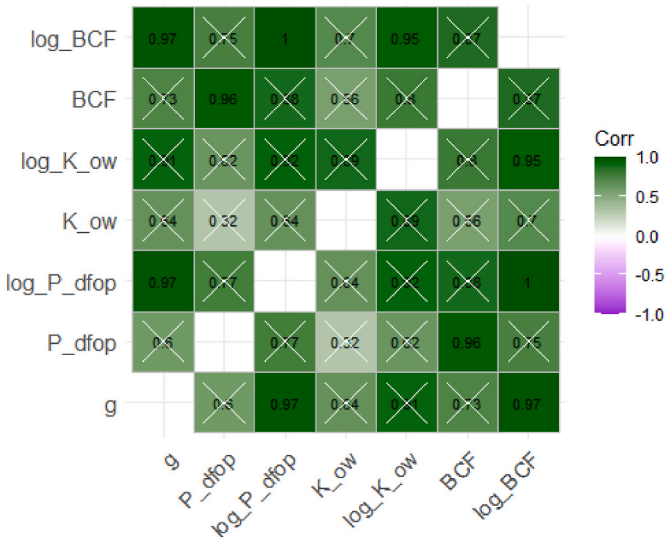


Fig. 3. Pearson's correlation matrix between selected environmental fate indexes. g = DFOP parameter, P_dfop = g/(1-g), log_P_DFOP is the logarithm (base 10) of P_DFOP, K_ow = octanol-water partition coefficient, log_K_ow = logarithm (base 10) of K_ow, BCF = bioconcentration factor, log_BCF = logarithm (base 10) of BCF. Non-significant (alpha >5%) correlations are X-crossed.

The interpretation of the possible meaning of the *g* parameter is rather complex. The DFOP model assumes that most of pesticide undergoes two simultaneous dissipations in two different compartments, hence it is split into two fractions: *g* and (*1-g*). Given that the FWS CW sediment did not contain detectable amounts of pesticides, it is reasonable to assume that the two sub-compartments considered by DFOP must be confined within the submerged water column, possibly a distinct part of the aqueous ecosystem such as the water itself, microbiota, or vegetation. A simple speculative hypothesis may relate *g* and (1-*g*) fractions to: (i) the water mass, and (ii) the biomass, such as the plant roots and debris, algae, mucigel, micro and macro-organisms, along with all bio-interfaces capable to sequestrate or internalize hydrophobic species from water.

Possible clues to verify this hypothesis were searched by evaluating correlations between the *g*/(1-*g*) ratio and pesticides' environmental fate indexes, namely: *n*-octanol/water partition coefficient (K_{ow}), and the bioconcentration factor (BCF).

The g/(1-g) ratio was better described as P_{DFOP} by the following Eq. (5):

$$P_{DFOP} = \frac{g}{(1-g)} \quad \text{Eq. 5}$$

P_{DFOP} equaled 10.76, 3.504, 75.92 and 17.52 for acetamiprid, metalaxyl, metolachlor and terbuthylazine, respectively.

As far as K_{ow} was concerned, considering that metalaxyl, metolachlor and terbuthylazine have log K_{ow} higher than 1 (Table 1), it is possible to speculate that *g* (always larger than 1-*g*), hosting the faster degradation, could represent the biomass-bound fraction of the three pesticides. On the contrary, the value of log K_{ow} lower than 1 for acetamiprid indicated the water environment as the one containing the main g fraction of the pesticide, owing to its hydrophilic nature. For metalaxyl, metolachlor and terbuthylazine, the correlations between P_{DFOP} and partition coefficients of interest to the scope of environmental fate of pesticides, such as the already mentioned K_{ow} or BCF was evaluated. In the case of acetamiprid, given its high hydrophilic behavior (K_{ow}<1) and BCF of

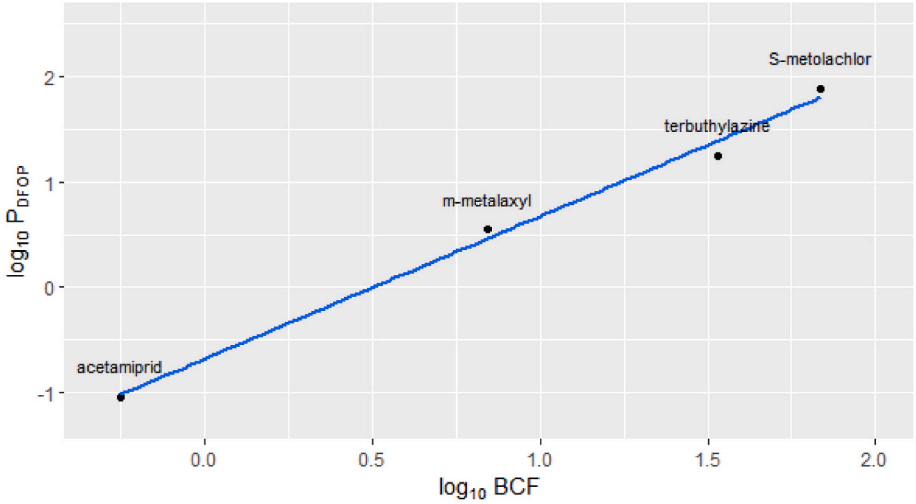


Fig. 4. Plot of $\log_{10}P_{DFOP}$ versus $\log_{10}$BFC for the considered compounds.

0.56 computed in tadpoles (Guo et al., 2022), the reciprocate of P_{DFOP} was used, as the larger sub-compartment g is the "hydrophilic" one, whilst the opposite is true for the other molecules. Pearson's correlation matrix between P_{DFOP} (or its reciprocate for acetamiprid) and K_{ow} or BCF indexes of the four pesticides are reported in Fig. 3. Interestingly, the reported K_{ow} or BCF of the pesticides highly correlated to the partition coefficient P_{DFOP} (its reciprocate for acetamiprid) resulting from DFOP model fitting.

In Fig. 4 it is possible to visualize the excellent relation between BCF and P_{DFOP}, having an adjusted coefficient of determination (R^2) = 0.9891 and a significance p = 0.004. These results are far from conclusive, due to the low number of observations (n = 4) and considering that BCF of an active compound is species-specific and can significantly vary upon organism size, lipid content and species (Arnot and Gobas, 2006). Nevertheless, the high correlation between K_{ow}/BCF and P_{DFOP} of pesticides with organophilic nature, as well as the reciprocate P_{DFOP} of acetamiprid, allowed to obtain some clues to better understanding the dissipation of pharmaceuticals in biologically active water bodies, suggesting a decisive role of biota in dissipating active compounds. Organophilic pesticides with high BCF and K_{ow} (metalaxyl, metolachlor and terbuthylazine) may be primarily dissipated though organism's assimilation or internalization, while acetamiprid dissipated or degraded in the water phase (e.g., by hydrolysis) accordingly to environmental parameters

Picture 1. A: Satellite picture of the free water surface constructed wetland (green line), served farmland (light blue line) and the main ditch (dashed black line). 1 B: aerial view of the free water surface constructed wetland. For reference, the north corner is marked with a white asterisk on both pictures A and B.

Even considering the most conservative endpoints resulting from acceptable fitted models, the dissipation of half of initial pesticide mass occurred at a fraction of those reported in literature (see Table 1, AERU, 2023), within the considered CW. Particularly, metalaxyl halved in 5.8–8.0 days, whereas official repositories indicate a DT_{50} in water of 56 days. This is a further indication that the FWS CW acted similarly to a bioreactor, due to its ecological characteristics. In the light of these considerations, as a final remark, it should be underlined that such nature-based systems have a limited resistance to stressors and cannot be treated as chemicals dumpsters only because they can be rather efficient in degrading pesticides. Such abuses compromise their capacity to remove nutrients and contaminants, as well as pejorate biodiversity at larger scale.

4. Conclusions

Agricultural runoff and drainage water pollution due to pesticides occur when these chemicals, used in farming to protect crops from pests and diseases, are carried by water runoff or leach into surrounding water bodies. The runoff can result from rainfall, irrigation, or excessive watering, transporting pesticides from fields into nearby streams, rivers, lakes, or groundwater, causing their pollution.

CWs serve as vital ecosystems that support a diverse array of life and provide various ecological niches. Besides that, during exceptional events such as heavy rain or flooding, CWs play a crucial role in acting as a buffer, safeguarding downstream water bodies from contamination by effectively filtering and degrading nutrients and contaminants originating from agricultural activities.

This research focused on assessing and modeling the capacity of a vegetated free water surface (FWS) CW to mitigate pesticide-

contaminated agricultural runoff and drainage water within a farm-scale rural setting. The mature FWS CW studied was effective in retaining >99% of pesticides mass and dissipated 90% of initial load of acetamiprid, metalaxyl, S-metolachlor and terbuthylazine within 8.7, 26.6, 5.1 and 7.8 days, respectively. Except for the case of metalaxyl, more than 90% of introduced pesticides were degraded before the CW had the chance to fill up and produce outflow. These findings highlight that, beyond its effectiveness in preventing leaching and contamination of water bodies, the CW demonstrated a faster removal of pesticides than most of other CW systems or pilots reported in previous literature (despite the difficulties of a reliable comparison). The research showed that nonlinear kinetic models performed better in describing the dissipation of acetamiprid, metalaxyl, metolachlor and terbuthylazine. Particularly, DFOP kinetic model was the best fitting, and it was observed that its partition parameter *g* was partly related to the four pesticides tabulated K_{ow} and BCF.

Kinetic models (e.g., SFO, FOMC, DFOP) can serve as valuable tools to predict pesticides dissipation in CWs. However, these models have certain limitations stemming from their simplification of complex processes, reliance on assumptions about pollutant behavior, and the variability inherent in CW designs and pollutant types. Factors such as temporal variations, site-specific variability, and the complexity of pollutants can challenge the accuracy and applicability of these models. While they provide useful insights, their effectiveness is contingent upon proper calibration, validation, and supplementation with empirical data and field observations. Therefore, a comprehensive understanding of the specific wetland system under study remains crucial to augment the reliability of these models for predicting pollutant dissipation in CWs.

Compliance with ethical standards

The research activities described in this paper do not involve any human or animal participants.

Utilization of generative AI

During the preparation of this work the author(s) used ChatGPT 4.0 in order to Improve readability and language. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Consent to publish

All authors have read and approved this manuscript and gave their consent for publishing.

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CRediT authorship contribution statement

Enrico Buscaroli: Writing - review & editing, Writing - original draft, Methodology, Formal analysis, Data curation. **Stevo Lavrnić:** Writing - review & editing, Methodology, Conceptualization. **Sonia Blasioli:** Methodology, Conceptualization. **Salvatore Luca Gentile:** Writing - review & editing, Methodology, Data curation. **Domenico Solimando:** Methodology, Conceptualization. **Giuseppe Mancuso:** Writing - review & editing. **Stefano Anconelli:** Supervision, Resources, Methodology, Conceptualization. **Ilaria Braschi:** Writing - review & editing, Supervision, Resources, Methodology, Conceptualization. **Attilio Toscano:** Writing - review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2024.118275.

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