

Potential of barrage fish ponds for the mitigation of pesticide pollution in streams

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Abstract

Barrage fishponds may represent a significant surface water area in some French regions. Knowledge on their effect on water resources is therefore necessary for the development of appropriate water quality management plans at the regional scale. Although there is much information on the nutrient removal capacity of these water bodies, little attention has been paid to other agricultural contaminants such as pesticides. The present paper reports the results of a 1-year field monitoring of pesticide concentrations and water flows measured upstream and downstream from a fishpond in North East France to evaluate its capacity in reducing pesticide loads. Among the 42 active substances that had been applied on the fishpond's catchment, seven pesticides (five herbicides, two fungicides) were studied. The highest concentration in the inflow to the pond was 26.5 µg/L (MCPA), while the highest concentration in pond outflow was 0.54 µg/L (prosulfocarb). Removal rates of dissolved pesticides in the fishpond.

Introduction

Pesticides are used worldwide to control various pests (United Nations Environment Programme 1998). Herbicides, fungicides, and insecticides used in Europe (European Union, 25 member states) account for up to 210,000 t of active ingredients (a.i.) applied on about 178.8 millions of hectares of agricultural land resulting in an average application dose of 1.2 kg a.i./ha (European Environment Agency 2005). France is the first market for pesticides in Europe and accounts for 28 % of the plant protection products used in European Union with an average application dose of 2.3 kg a.i./ha of agricultural land (Le Gall et al. 2013). Substantial amounts (0.1–10 %) of the applied pesticides might be lost to surface waters via surface and subsurface runoff, tile drain flow, and spray drift (e.g., Garmouma et al. 1997; Kreuger 1998; Leu et al. 2004; Ng and Clegg 1997; Tediosi et al. 2012). According to the literature, the highest pesticide runoff losses generally occur during the first few rainfall events that follow pesticide application. Such studies show that weather conditions, soil type, slope, land use, application dose, and sorption behavior of the compounds are crucial factors influencing the overall pesticide losses from a catchment (Holvoet et al. 2007). These pesticide loads contribute to local and regional contamination of surface waters (French Ministry of Ecology and Energy 2013; Lazartigues et al. 2012; Lazartigues et al. 2013a, b; Loos et al. 2009). Measured pesticide concentrations

can be above the environmental quality standards set by the Water Framework Directive (WFD) of the European Union (2000).

When pesticides enter the aquatic environment, they are subjected to different physical, chemical, and biological processes that might result in compound degradation. Constructed wetlands and vegetated ditches have been suggested as potential measures for controlling non-point source pesticide pollution thereby restoring the ecosystem services that were lost after natural wetlands were drained and converted into agricultural lands (Budd et al. 2009; Haarstad and Braskerud 2003; Lizotte et al. 2012; Maillard et al. 2011; Maillard and Imfeld 2014; Matamoros et al. 2012; Moore et al. 2002; Passeport et al. 2013; Schulz et al. 2001; Tournebize et al. 2013; Vymazal and Březinová 2015). Therefore, constructed wetlands offer benefits, and implementing such systems is encouraged in order to achieve the good chemical status required by the WFD. In the aquatic environment, the two processes which have a major impact on the fate of pesticides are considered to be sorption–desorption processes and biodegradation. In constructed wetlands, Stehle et al. (2011) showed that removal rates of pesticides were related to pesticide properties such as organic carbon sorption coefficient (KOC) and water phase 50 % dissipation time (DT₅₀ water). Relevant properties of the constructed wetland to explain varying removal rates included hydraulic retention time (ØT) (i.e., the system volume divided by the flow of water) and plant cover (%) (Stehle et al. 2011). Both characteristics may be related to the reduction of flow velocity and enhanced sedimentation.

Barrage fishponds are man-made shallow water bodies generally located on headwater streams and associated to agricultural or forested catchments. In France, fishponds represent a surface area of more than 112,000 ha, and their use for fish production is longstanding practice. Barrage fishponds were built as early as 1220 by monks who dammed small streams to practice extensive polyculture with common carp as the emblematic species (Billard 2010). Regions with a high density of ponds can be found in Lorraine, Dombes, Brenne, Forez, Bresse-Jura, or Franche-Comté (Wezel et al. 2013). In order to maintain ecological continuity of streams, the removal of dams is currently promoted (European Environment Agency 2012; French National Agency for Water and Aquatic Environments 2010). Before further actions are taken, a greater knowledge of the influence of these water bodies on water resources, including water quality, is needed. While the effect of fishponds has been evaluated for traditional macropollutants (nitrogen, phosphorus) (Banas et al. 2002; Banas et al. 2008), it has not been evaluated for the relatively recently legislated micropollutants of the Water Framework Directive such as pesticides (European Union 2008, 2013). Considering that barrage fishponds and constructed wetlands have similar properties such as high HRT and large development of associated vegetation, fishponds could have a potential for the treatment of diffuse sources of pollution. The objective of the present study was to assess the efficiency of a fishpond fed by agricultural runoff to reduce loads of pesticides applied on its catchment.

Material and Methods

2.1. Study area

The Lorraine Region is located in the upstream part of the Rhine River basin (48° 45' N, 6° 44' E; Fig. 1). It has a high density of fishponds covering around 7,000 ha and managed to produce 1,100 t of fish yearly (Le Quéré and Marcel 1999; Lorraine Chamber of Agriculture 2005). Management operations of fishponds in the Lorraine Region include (i) a draining step, every 1 to 3 years to allow fish harvest; (ii) a filling step during which pond level increases as a result of water inputs from streams, runoff from surrounding areas, and direct precipitation; and (iii) a pseudo-balance step during which the pond is more or less full depending on the water balance and fish can be stocked and grown. As most fish farmers practice extensive polyculture, additional feeding and use of fertilizers or pesticides in ponds are not a common practice in the area (Chary 2013).

A barrage fishpond of the Lorraine Region was selected based on the following criteria: (i) pond draining agricultural land treated with pesticides; (ii) water mainly supplied by streams, easier to monitor than runoff; and (iii) HRT representative of the range observed in the Lorraine Region. As no study regarding HRT of barrage fishponds in the region was available, we used surface areas of ponds and

associated catchments as a proxy for HRT. From a sample of 105 ponds located in the Lorraine Region, the median pond surface (25th/75th quartiles) was estimated at 5.4 ha (2.5/18.0) associated with a median catchment supplying these ponds of 168.2 ha (75.8/489.2) (unpublished data).

The studied fishpond was located in the Saulnois area (in the southern part of the Moselle department; Fig. 1). The pond surface area was 4.4 ha associated to a catchment surface of 86.2 ha (Table 1). The volume of the fishpond was estimated through bathymetry at 44,000 m³ (Lazartigues 2010). The water body covered 5.1 % of its catchment compared to a median of 3.2 % for ponds in the Lorraine Region and was therefore expected to be in the range of relatively high HRT. The mean pond depth was 0.9 m with a maximum of 2.2 m measured at the dam (Lazartigues 2010). Water inputs to the barrage pond included inflow from a single tributary, direct precipitation, surface runoff from surrounding areas, and groundwater seepage. Water outputs included evapotranspiration, seepage, overflow, and regulated discharge during draining operation (Boyd and Gross 2000). Exchange with groundwater was however limited by the heavy clay soils and impermeable Keuper marls substratum on which the fishpond was built (French Geological Survey 2001).

Dominant soil types in the catchment were acidic Luvisol and gleyic Cambisol (Brethes 1976). The fishpond's catchment was covered by permanent pastures for livestock (42.5 ha), and arable land (33.9 ha) and the last fraction of land were used as roads and buildings (Fig. 1). A surface of 13.2 ha was artificially drained. Among arable lands, the cultivated surface areas and the proportion of crop variety varied annually as follows. The farmers mainly grew rapeseed (*Brassica napus* L.), wheat (*Triticum aestivum* L.), and barley (*Hordeum vulgare* L.) in a 3-year cultural rotation as commonly practiced in the region (Xiao et al. 2014).

2.2. Pesticide application and selection

Information on crops, pesticide handling, and use at the field scale (i.e., type of pesticide, quantity applied, date of spraying, field location) was collected through personal interviews with the farmers. During the investigation period, 42 different active substances were applied on the fishpond's catchment, dominated by herbicides (n=26), fungicides (n=11), insecticides (n=4), and molluscicide (n=1) (see Supplementary material, Table S1 for complete list of the applied substances). The total amount of pesticides applied on the fishpond's catchment was 84 kg a.i. The yearly application rate per hectare of arable land were indeed 2.1 kg a.i. for herbicides, 0.3 kg a.i. for fungicides, 0.02 kg a.i. for insecticides, and 0.06 kg a.i. for molluscicides. With 1,210 t of active substances applied annually on 694,000 ha of arable land in the Lorraine Region, these local application rates were higher than the regional average application rate of 1.7 kg a.i./ha (Agreste 2013; Regional Action Group Against Pesticide Water Pollution in Lorraine 2006).

Among the 42 applied active substances, seven pesticides (clethodim, clopyralid, fluroxypyr, MCPA, prosulfocarb, boscalid, propiconazole) were studied for the following reasons: (i) They represented normal pesticide use in the region (Moselle Chamber of Agriculture, personal communication). (ii) As the sampling station to monitor pesticide inputs to the pond was located upstream from the pond, the pesticides selected were those almost exclusively applied on the catchment drained towards the upstream location (i.e., quantity applied on the catchment drained to upstream location $\geq 90\%$ of the total quantity applied on the fishpond's catchment) (Fig. 1). Among the 42 applied active substances, 13 pesticides were selected according to these criteria. It was therefore assumed that the majority of the pesticides load would pass through the monitored upstream point. For the selected pesticides, the inputs from runoff on agricultural areas around the plot (not monitored) were then considered negligible. (iii) The selected pesticides were analyzed using the same methodology. Among the 13 pesticides almost exclusively applied on the catchment drained to upstream location, eight could be analyzed using the same method. (iv) Lastly, the frequency of quantification (i.e., number of samples above the quantification limit over the number of total samples) was above 10% for seven selected pesticides at the upstream or downstream locations, while one pesticide (propaquizafop) was never detected. Indeed, a large number of non-detected/non-quantified precludes estimation of actual pesticide loads (Guo et al. 2004).

The seven pesticides selected were applied on the three main crops grown in the area, i.e. rapeseed, barley, and wheat. Rapeseed was treated in mid-September with the

post-emergence herbicide clethodim (48 g a.i./ha) and at the beginning of May with the fungicide boscalid (145 g a.i./ha). Spring barley was treated in April with the fungicide propiconazole (70 g a.i./ha) and at the beginning of June with three herbicides (clopyralid, fluroxypyr, and MCPA) at rates of 36, 72, and 360 g a.i./ha, respectively, components of the same commercial product. Winter wheat was sprayed with prosulfocarb at the end of October at a relatively high rate (2,160 g a.i./ha).

2.3. Water sampling and measurements

The sampling campaign was conducted during 1 year from March 2013 to March 2014. The monitoring stations were located upstream and downstream from the fishpond (Fig. 1). As surface water flow may be bidirectional in the main tributary, usually controlled by water level fluctuations in the pond, the upstream point was located far enough from the pond to sample exclusively water flowing to the pond. At each station, a 90-V notch weir (Castorama, France) was installed and equipped with a water level measurement device composed of a pressure sensor. Data was recorded every 15 min by a data logger Hawk XT (Isodaq Technology, UK). The water level was converted into stream flow by a station-specific rating curve obtained from periodic discharge measurements using either a bucket for water flow below 5 L/s or a current meter when water flow was above.

Twenty-four-hour composite water samples were collected approximately every 2 weeks. A total of 52 samples was analyzed including 26 samples upstream and 26 samples downstream. As no power source was available on-site, the use of refrigerated samplers during summer or heating devices during winter was not possible. The following sampling strategy was therefore designed to minimize latency between sampling and extraction time. Water samples were collected twice a month at the two stations using a SIGMA SD 900 portable automated sampler (Hach Lange, France) programmed to obtain a 24-h composite sample (hourly aliquots) collected in a single polyethylene flask. Samples were retrieved within a few hours after collection of the last sample, transferred into 1-L amber glass bottle, and kept in the dark at 4 °C before being processed. Extraction occurred within 48 h to avoid possible loss of compounds from the dissolved phase by sorption or degradation during sample storage. In an evaluation of sorption and degradation of pesticides in polyethylene flask having similar properties than the studied compounds, Rabiet et al. (2010) determined that losses were below 10% over a 2-day period. We assumed that the short period of storage did not result in significant transformation of either pesticides, although no in-bottle stability tests were performed. This is considered in the interpretation of the results.

Temperature, dissolved oxygen, pH, and conductivity were directly measured in the streams at the time of sample collection using a portable data logger connected to multiple probes (Odeon, Neotek-Ponsel, France). Measures of total suspended solids (TSS) and volatile suspended solids (VSS) in water samples were made in the laboratory according to standard methods (American Public Health 1998).

2.4. Pesticide analysis

To estimate the water contamination by pesticides, the WFD focuses on the dissolved phase as dissolved contaminants are considered available but also because of analytical difficulties in analyzing the fraction of pesticides sorbed to sediments. In the present study, only the dissolved phase was examined as previously reported (e.g., Palma et al. 2004; Gregoire et al. 2010).

Detection and identification of the dissolved pesticides was realized using liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) with multiple reaction monitoring. Before injection, water samples were centrifuged 15 min at 14,000 rpm at 4 °C to eliminate the suspended solids. On-line enrichment of targeted compounds was performed on a HypersilGold column (20x2.1 mm i.d., with 12 µm particles) (Waters Corporation, Manchester, UK). For each sample, 1,400 µL was injected through this column. The loading run time was set to 2 min at a flow rate of 2 mL/min. Then, compounds retained in the cartridge were progressively transferred to the chromatographic column with acidified water (0.05 % formic acid). Liquid chromatography was performed using a Waters Acuity UPLC® system (Waters Corporation, Manchester, UK) coupled to a Waters Xevo® TQ mass spectrometer for identification and quantification. Chromatographic separation was achieved using a BEH C18 (150x2.1 mm i.d., with 1.7 µm particles). A binary mobile phase consisting of 0.05 % formic acid aqueous solution (A) and 0.05 % formic acid acetonitrile solution (B) was used. The elution/separation gradient started at 100 % aqueous solution (A), followed by an 8-min linear gradient to 50 % A and the final gradient change to 100 % solution B in 14 min. The column was equilibrated for 4 min prior to the next analysis. The flow was 0.4 mL/min, and the total run time was 18 min. Every sample was analyzed in duplicate to verify the repeatability, and two blank samples were injected after every sample to avoid cross-contamination. Recoveries were evaluated by spiking each sample at two concentration levels (limit of quantification and the highest calibration point). Dilutions of heavily contaminated samples were performed. Limits of quantification (LQ) varied between 0.004 and 0.1 µg/L, and average spike recovery ranged between 48 and 120 % (see Table S2 in the supplementary material for LQ, spike recovery, and uncertainty measurements for the seven compounds).

2.5. Efficiency assessment and removal processes

2.5.1. Removal rates

The mass of a substance S in the pond is influenced by (i) external processes (inflow, outflow), (ii) internal exchange processes (sediment/water exchange, air/water exchange), and (iii) internal transformation processes which include chemical, photochemical, and biological transformations.

In the present study, the efficiency of the fishpond in removing pesticides from the water column was assessed by using the pesticide load reduction rate, RL (%), calculated on an annual basis (Budd et al. 2009; Maillard et al. 2011; Passeport et al. 2013; Tournebize et al. 2013):

$$R_L(\%) = \frac{L_{S,in} - L_{S,out}}{L_{S,in}} \times 100$$

with $L_{S,in}$ being the load of an individual substance S entering the pond (upstream location) and $L_{S,out}$ the load of an individual substance S leaving the pond (downstream location). As explained earlier, the selected pesticides had mainly been applied on the catchments drained to the upstream sampling location. The loads estimated at this point were therefore considered to represent the large majority of the actual pesticide load entering the pond. Data below the limit of detection were replaced with zeros, and data below the LQ were replaced by LQ divided by 2 (Passeport et al. 2013).

2.5.2. Selecting a calculation method to estimate pesticide loads

The load of a substance S transported by the pond inflow or outflow is the product of the water discharge and the concentration of that substance in the water flow. Such calculations inevitably introduced uncertainty as the concentrations were only obtained punctually while continuous records of water discharge were usually available. A wide range of methods have been suggested to calculate stream loads from concentrations and flow data using interpolation methods (based on the assumption that the measured concentration is representative of conditions in the stream during the periods between samples) and extrapolation methods (based on correlations between contaminant concentrations and streamflow) (e.g., Cohn 1995; Johnes 2007; Littlewood 1995; Quilbé et al. 2006; Walling and Webb 1985). These methods have been suggested to estimate sediment and nutrient loads transported by streams (Johnes 2007; Quilbé et al. 2006; Walling and Webb 1985) and more rarely to estimate pesticide loads (Boithias et al. 2011; Guo et al. 2004; Rabiet et al. 2010).

Due to differences in the temporal variability of pesticide concentrations, different calculation methods were applied to the upstream and to the downstream datasets. Because of direct link to surrounding agricultural areas and limited dilution potential by other water sources, the pesticide concentrations were hypothesized to be highly variable in the inflow water, with highest concentrations measured during post-application runoff events (Gøoøet al. 1997; Leu et al. 2004; Rabiet et al. 2010). The variability of chemical concentrations was assumed to be strongly reduced in the pond outflow (Blankenberg et al. 2006; Lizotte et al. 2012).

2.5.3. Estimation of pesticide loads in the pond inflow

At the upstream location, it would have been relevant to apply an extrapolation procedure involving empirical relationships between pesticide concentrations and stream flows due to the dynamic of pesticides in headwater streams. However, there was no linear relationship between concentrations and discharge measured upstream from the

pond. Three different interpolation procedures were therefore used to estimate pesticide loads at the upstream location.

In a first procedure, a flow-averaged mean load was calculated for the sampling days, which was then corrected by the total water discharge during the investigation period (Gómez-Gutiérrez et al. 2006; Walling and Webb 1985):

$$L_S = \frac{365 \sum_{i=1}^n (0.001 \times C_i Q_i)}{\sum_{i=1}^n Q_i} \bar{Q}_r$$

where L_S (g/year) is the load for the substance S , n the number of samples, C_i ($\mu\text{g/L}$) the concentration value at the time of sampling, Q_i (m^3/day) the discharge at the time of sampling, and \bar{Q}_r (m^3/day) the mean discharge during the period of record.

In the second procedure, the load of pesticides was calculated by multiplying the average stream flows measured during the period between sampling days by the pesticide concentrations measured on the sample as suggested by Rabiet et al. (2010):

$$L_S = 0.001 \left(\sum_{i=1}^n C_i \overline{Q_{i, i+1}} \right)$$

where $Q_{i, i+1}$ (m^3/day) is mean discharge for the period between sampling dates i and $i+1$.

In the third procedure, a linear interpolation method was applied for concentrations between neighboring sampling points, often applied to calculate pesticide loads (Boithias et al. 2011; Guo et al. 2004). No interpolation was made between sampling dates before and after application. The continuous daily loads were calculated though the multiplication of daily concentrations and daily discharges. This method has often been applied to calculate pesticide loads.

$$L_S = 0.001 \sum_{j=1}^{365} C_j^{\text{int}} Q_j$$

where C_j ($\mu\text{g/L}$) is the linearly interpolation concentration, and Q_j (m^3/day) is the measured daily discharge.

The minimum and maximum load estimates calculated according to these three procedures are presented in Table 4.

2.5.4. Estimation of pesticide loads in the pond outflow

In the pond outflow, the variability of pesticide concentrations was lower and calculation methods were as follows. Before the observation of pesticide peak concentrations in pond outflow, concentrations were linearly interpolated and loads were calculated as presented in Eq. 4. After the occurrence of the peak concentration, pesticide concentration values were expressed as a first-order reaction. The characteristic rate constants for each pesticide were calculated by fitting the concentration data to the first-order decay model as suggested by Ulrich et al. (1994):

$$C_j = a e^{-kt}$$

where C_j is the interpolated concentration, a is a constant, and k is the characteristic rate constant of the first-order reaction. Daily concentrations were then multiplied by daily discharges to calculate loads.

2.5.5. Removal processes

When calculating the pesticide load reduction rate, the pond was considered as a black box and the importance of internal processes was not directly measured. The relative importance of each of the internal processes (e.g., sorption, volatilization, photolysis, hydrolysis, biotransformation) was assessed by comparison of key properties of the substances (Table 2). Possible significant differences among hydrological and hydrochemical parameters between upstream and downstream locations were detected by means of non-parametric paired Wilcoxon signed rank test using the R software (R Development Core Team 2005). Correlation between these parameters and pesticide metrics was tested by the rank-based Spearman's test.

Results and Discussion

3.1. Hydrological and hydrochemical context

Average annual air temperature during the investigation period was 10.1°C , which is lower than the 30-year average of 10.7°C . The monthly average air temperatures ranged from a minimum of 3.9°C in December to a maximum of 20.6°C in July. Total annual precipitation during the investigation period was 946 mm compared to a 30-year average annual precipitation of 800 mm (Château-Salins, Meteo France 2011). Spring and autumn seasons were particularly wet (159 , 116 , and 138 mm for the months of May, September, and October versus 30-year averages of 78 , 59 , and 68 mm , respectively). Twenty-nine rainfall events above 10 mm

occurred during the investigation period with highest rainfall events on May 3 (30 mm) and September 7 (36 mm). The summer months were relatively dry, precipitation values being in the lower range (67 mm in June and 37 mm in July versus 30-year averages of 83 and 61 mm , respectively). The annual evapotranspiration for the investigated period estimated from Penman-Monteith equation was 860 mm compared to a 30-year average of 778 mm (Château-Salins, Meteo France 2011). Evapotranspiration was the highest in the month of July (141 mm) and the lowest in December (9 mm).

Annual hydrological data is provided in Table 1, and temporal variation of stream inflow and pond outflow is provided in Fig. 2. During the spring high flow period (from March 25, 2013 to July 6, 2013), the pond was full and the average daily flow rates were 268 m³/day (0.62 mm/day) upstream and 472 m³/day (0.55 mm/day) downstream. During the low flow periods (approximately 2 months from July 7, 2013 to September 6, 2013), the pond level decreased as upstream flow rates were low (12 m³/day or 0.03 mm/day on average), and water losses from the pond occurred through evapotranspiration and leakage with a downstream flow rate of 32 m³/day (0.04 mm/day). During the autumn and winter high flow period (from September 7, 2013 to March 15, 2014), the average daily base inflow increased to 328 m³/day (0.76 mm/day) leading to increased pond water level until the opening of the water gate by the fishpond farmer. Indeed, pond outflows were the highest during draining operation (from November 27 to December 3, 2013) with 42,372 m³ released. After approximately 2 months, the pond was filled (from December 4, 2013 to February 11, 2014) (Fig. 2).

The theoretical residence time is often expressed as the volume of the water body divided by the outflow rate. The estimated HRT, obtained by dividing fishpond volume (m³) by yearly outflow (m³/year), was 97 days. Highest HRT were expected when the outflow rate was low (i.e., from July to September and from December to February), while lowest HRT were expected when outflow rate increased (i.e., spring and autumn high flow periods as well as draining operation). As mentioned earlier, HRT is among the most important determinant for pesticide reduction performance in constructed wetlands (Stehle et al. 2011). The period that water remains in a surface water body controls the time available for critical biological and chemical reactions to occur. In comparison to the theoretical HRT calculated for the studied fishpond, reported HRT for constructed wetlands, designed for the removal of pesticides, are much lower (varying between 0.04 and 27 days). The constructed wetlands represented less than 1 % of their watershed (Schulz et al. 2001; Braskerud and Haarstad 2003; Blankenberg et al. 2006; Budd et al. 2009; Passeport et al. 2013). Therefore, it seems that ponds have a great hydraulic potential to achieve the pesticide reduction objective. It should however be noted that theoretical HRT are probably an overestimation due to the existence of stagnant zones or short-circuit flow paths from inlet to outlet location, which will decrease the actual water residence time (Kadlec 2005).

Detailed hydrochemical data is provided in Table 3 (see supplementary material, Fig. S1 for time series of hydrochemical parameters). Dynamics of hydrochemical parameters measured upstream reflected catchment hydrogeology, while parameters measured downstream from the pond reflected hydrological and biogeochemical conditions within the pond. Temperature, dissolved oxygen concentration, electrical conductivity, and total suspended solids differed significantly between the upstream and downstream locations ($p < 0.05$). The pH ranged between 7.0 and 8.5 with no significant spatial differences. The lowest temperature (3.8 °C) was measured upstream in March, and the highest temperature (23.6 °C) was measured downstream at the end of July. Dissolved oxygen was generally lower downstream compared to upstream from the pond, especially in the summer months. The lowest dissolved oxygen concentrations were measured

downstream from the pond in July and August with a minimum of 1.7 mg/L indicating the prevalence of anoxic conditions. During the summer months, intensive decomposition of organic matter may lead to the development of anoxic conditions (Avnimelech and Ritvo 2003). Electrical conductivity, which is an indicator of the concentration of total dissolved ions, was generally higher upstream. However, a strong decrease in conductivity and increase in TSS were observed upstream in May. This reduced conductivity and increased TSS may be due to the input of runoff water with a low conductivity in the stream (Spalding and Snow 1989). Similarly, several increases in conductivity were observed downstream at the end of the summer and during winter. The TSS and VSS were generally higher upstream, although peaks of suspended solid were observed during the emptying operation as previously reported (Banas et al. 2002). Other key variables controlling pesticide removal mechanisms are changes of redox conditions or macrophyte development, but the evolution of these characteristics was not followed (Maillard et al. 2011).

3.2. Pesticide inputs

The highest concentrations for the seven selected pesticides were measured upstream. The maximum value was measured for the herbicide MCPA (26.5 µg/L), while the highest fungicide concentration was measured for boscalid (1.4 µg/L). Figure 2 illustrates the transport pattern of these two pesticides upstream and downstream of the studied fishpond by plotting pesticide concentration, discharge, and pesticide application during a year. Transport patterns of the seven pesticides can be found in the supplementary material (Fig. S2). Figures 2 and S2 show that concentrations were generally higher in the first flows following pesticide application. These high concentrations were associated with a significant increase in upstream load. Measurements of high pesticide concentrations in the first rainfall events following application and the associated increased pesticide loads have previously been reported by several authors (Leu et al. 2004; Ng and Clegg 1997). The high concentrations were correlated with the main agricultural pesticide application periods for rapeseed and cereals, which are May/June and August/September/October (Regional Action Group Against Pesticide Water Pollution in Lorraine 2006). Peaks of MCPA, clopyralid, and prosulfocarb (herbicides applied on cereals) were observed in May/June and November. Peak of clethodim (herbicide applied on rapeseed) was observed in September (see supplementary material, Fig. S2). Concerning fungicides, peaks of boscalid and propiconazole (fungicides applied on rapeseed and cereals) were recorded in May. Highest concentrations of fluroxypyr (herbicide applied on cereals) were measured between June 2013 (post-application sampling) and January 2014, which was unexpected considering the estimated field half-life of 51 days (Table 2) or the short field half-life (1 to 3 weeks) reported previously (Lehmann et al. 1991). However, pesticide field half-lives are dependent on soil properties, and the values presented in Table 2 may not be fully representative of the actual conditions in the studied catchment during the investigation period (Clavet 1995). Because of the lack of relationships between fluroxypyr concentrations and the recorded hydrochemical parameters, no assumptions could be made regarding the processes involved in fluroxypyr transport in streams.

The quantities of pesticides applied on the catchment studied and the measured loads at the upstream location are summarized in Table 4. The pesticide load measured at the upstream location indicates that only a small percentage of the applied pesticides is transferred from agricultural soil to surface waters. The relative loss from the field varied between 0.1 % (prosulfofcarb) to 9.8 % (MCPA). Among the seven substances, the largest field losses were observed for highly hydrosoluble pesticides (i.e., MCPA, fluroxypyr, clopyralid, clethodim; $K_d < 2$), likely corresponding to the molecules that are very mobile via dissolved phase. In contrary, the most sorbing molecules (e.g., propiconazole, prosulfofcarb, $K_d > 10$) showed lower upstream loads that might be consistent with retention by the soil in the catchment and/or a transport via particles. In small watersheds, it was estimated that on average, less than 2 % of the total mass of pesticide applied is ultimately loss to surface waters (Kreuger 1998; Leu et al. 2004). In a watershed of 22 ha, Haarstad and Braskerud (2003) observed an average loss rate of 4 %. The field losses observed in the present study can therefore be considered high. An explanation could be the high amount of rainfall that occurred during application periods leading to the fast transfer of pesticides through tile drains and surface runoff. Load estimates maybe strongly influenced by the sampling strategy and calculation methods implemented. In the present dataset, there was more than a 50 % difference in the magnitude of calculated loads between the three different methods (Table 4). If the dataset does not represent the entire range of flows and concentration values, underestimation and lack of precision are shown to be important problems (Rabiet et al. 2010). Indeed, at relatively low sampling frequencies, there is a high probability of missing the co-occurrence of high flow volume and high pesticide concentration. Since these high flow events will account for a substantial proportion of the total pesticide load, loading estimates based on low sampling frequencies are likely to underestimate the total annual load (Johnes 2007).

3.3. Removal efficiencies

At the downstream location, the concentration peaks were generally observed around 15 days after the upstream peak. The peak concentrations were of lower level in the outflow than in the inflow for the seven pesticides. The highest concentrations were observed for prosulfofcarb (0.54 $\mu\text{g/L}$) and MCPA (0.37 $\mu\text{g/L}$) (see Figs. 2 and S2 in the supporting information for maximal concentrations of the seven pesticides). Unlike concentration values collected in the pond inflow, the pesticide concentrations in the outflow, except for fluroxypyr, followed a first-order kinetic with a significant characteristic rate constant ($p > 0.001$). As observed at the upstream location, fluroxypyr concentrations in the pond outflow were highly variable with no significant correlations between concentrations and the recorded hydrochemical variables.

Load reduction varied between 0 and 8 % (prosulfofcarb) to 100 % (clopyralid). In comparison, retention rates of pesticides in constructed wetlands found in the literature are 27–93 % for MCPA (Braskerud and Haarstad 2003; Cheng et al. 2002; Matamoros et al. 2008) and 93 % for prosulfofcarb (Passeport et al. 2013). Differences in mitigation effectiveness among constructed wetlands could be attributed to varying HRT or plant cover and density (Stehle et al. 2011). As mentioned earlier, estimated HRT for the studied fishpond was 97 days, so in general, higher retention

rates in fishponds compared to constructed wetlands could be expected (Schulz et al. 2001; Braskerud and Haarstad 2003; Blankenberg et al. 2006; Budd et al. 2009; Passeport et al. 2013). This was confirmed for MCPA but not for prosulfofcarb. However, it should be kept in mind that potential bias to estimated removal rates calculated in the present study was related to (i) the low frequency (i.e., twice a month) of water sampling, which is even more problematic for the estimation of pesticide loads upstream due to strong temporal variability of pesticide concentrations; (ii) the location of the sampling stations, which did not allow to evaluate the pesticide load entering the pond from adjacent agricultural areas (i.e., direct runoff and subsurface runoff); and (iii) the possible in-bottle degradation and sorption of pesticides during sample storage. These first two aspects have presumably led to minimizing pesticide inputs therefore minimizing removal rates. Regarding the impact of in-bottle pesticide degradation and sorption on removal rate estimations, it should be considered that these processes occurred at both the upstream and downstream locations and that the samples were collected identically for both stations. Therefore, removal rates, calculated as a relative decrease of downstream pesticide loads to upstream loads, were presumably less affected by in-bottle transformation processes than the value of pesticide loads. In order to estimate removal rates more accurately, care should be taken to monitor all potential pesticide inputs (i.e., main tributary, runoff, subsurface runoff from agricultural fields adjacent to the pond). Additional samples should be taken during runoff events following pesticide application at these locations.

3.4. Removal processes

We studied the removal rates of seven different pesticides with contrasting properties (Table 2), application rate, and application period (Table 4). Pesticides are removed from the water column in the pond through many processes, but the most important processes are probably sorption and sedimentation, photolysis, hydrolysis, microbial degradation, and plant uptake (Vymazal and Březinová 2015). The extent of processes involved in pesticide removal depends on many factors such as organic matter content, clay content, pH, redox conditions

inputs of pesticide mass, or the presence and types of macro-phytes (Maillard et al. 2011; Maillard and Imfeld 2014). As both pesticide half-lives and sorption partitioning coefficients are dependent on water and sediment properties, the values presented in Table 2 may not be fully representative for different sites and periods of the year.

Clethodim, clopyralid, fluroxypyr, and MCPA are acid compounds. They should be present as their anionic forms at the pH of pond water ($pK_a < pH$, pH range = 7.0–8.4). Clay minerals usually display limited affinity for anionic pesticide species in relation to negatively charged clay surfaces (Lagaly 2001). In consequence, these pesticides were probably weakly retained by most sediment components and associated to dissolved cationic ligands (e.g., K^+ , Mg^{2+} , humic, and fulvic acids) in the water phase. Anionic pesticide species could therefore be easily degraded owing to high availability of dissolved substances for abiotic or biotic transformation processes (Ying and Williams 2000; Sevilla-Morán et al. 2010; Hu et al. 2014; Sura et al. 2015). Among the acid compounds, only MCPA and clethodim were subject

to rapid photodegradation in water (Table 2). MCPA was known to be quickly removed by photolysis processes in several conditions (i.e., natural freshwater, natural brackish water, and ligand associated; Al Housari et al. 2011), while pH and ligands (e.g., humid acids) in the turbid pond context might have affected clethodim photolysis rate (Falb et al. 1990; Sevilla-Morán et al. 2010). Dissolved organic matter and vegetation shading may have reduced the effect of photodegradation in ponds (Braskerud and Haarstad 2003). Only fluroxypyr could undergo hydrolysis under the conditions typically encountered in the water column of a pond (Table 2). The chemical hydrolysis of fluroxypyr was reported to be both pH- and temperature-dependent and accelerated by alkaline conditions and higher temperatures (Hu et al. 2014). In freshwater systems, high biodegradation rates were observed for MCPA and fluroxypyr while little information was available for clethodim and clopyralid (Al Housari et al. 2011; Lehmann et al. 1993). Some studies on cyclohexanedione oxime herbicides (CHD, family that includes clethodim) show that biotic degradation occurs in terrestrial environments (Ono et al. 1984). Given the properties of the acid pesticides, similar and high removal rates were expected for MCPA and clethodim, while lower removal rates were expected for clopyralid and fluroxypyr. However, the removal rate of clethodim was the smallest (RL=33–76 %) and clopyralid was the highest (RL=100 %). The low removal rate observed for clethodim could be attributable to a low photodegradation rate as explained above. It could also be explained by the application period of clethodim (autumn) while the other pesticides were applied in summer. Maillard and Imfeld (2014) suggested that during spring, plant uptake was the major dissipation process, while during summer and late summer, biodegradation and sorption on bed sediment prevailed,

respectively. As temperature decreased in autumn, lower biodegradation rates could be expected leading to a low removal rate of compounds (e.g., clethodim) applied during this period.

Contrary to the acid compounds, prosulfocarb (applied in October) and boscalid and propiconazole (applied in April/May) are relatively stable regarding physical and chemical degradations (Table 2). Biodegradation would be the main pathway for degradation, but it might be insufficient for prosulfocarb. Prosulfocarb presented the worst reduction with a RL of 0–8 %. Prosulfocarb was applied in October, when conditions for its biodegradation may not have been optimal (Maillard and Imfeld 2014). Unfortunately, the processes involved in pesticide degradation in aquatic ecosystems are poorly studied for these three substances, while some data was available regarding terrestrial systems. More particularly, the strong affinity of prosulfocarb for organic matter was already suspected to reduce its bioavailability and hence its biodegradation by microbial fauna (Gennari et al. 2002). Similar processes occurring in pond, such as complexation with dissolved organic matter together with decreased biodegradation during autumn, could explain low removal efficiency of prosulfocarb. For these three compounds, an important proportion of the transported pesticides may be in the particulate phase. The efficiency of the fishpond in removing sorbed pesticides should be evaluated as well. Care should be taken to sample storm events in the inflow and draining operation in the outflow during which major sediment export occurs (Banas et al. 2002).

Conclusion

The present study provides quantitative, field data on the capacity of fishponds to retain dissolved pesticides. The barrage fishpond could efficiently trap pesticides transported in runoff from agricultural fields. The retention rates for the chosen pond varied between 0 and 100 % depending on the substance. This lends credibility to the role of fishponds regarding pesticide mitigation. There were a number of limitations of the study described here which should be redressed in further work. Care should be taken to monitor all potential pesticide inputs and to increase sampling frequency, especially upstream of the pond. A mass balance study investigating pesticide occurrence in water, fish, sediments, and macrophytes into the fishpond could provide

additional insight regarding removal mechanisms as well as risk of ecotoxicity for the ecosystem (Moore et al. 2009).

Barrage fishpond culture is along-standing practice for fish production, and this original work shows that, although not purposely designed for the treatment of diffuse sources of pollutants, fishponds have a potential to do so and should be integrated in regional water quality management plans. The high water detention times of these systems suggest high retention rates. Further research effort could be conducted to improve and maximize their role in pesticide mitigation along with other ecosystem services (Aubin et al. 2014).

Table 1. Pond and catchment characteristics

Pond morphometry	
Area (m ²)	44,000
Volume (m ³)	44,000
Mean depth (m)	0.9
Maximum depth (m)	2.2 Pond
hydraulics	
Inflow (mm/year)	211
Outflow (mm/year)	173
Mean residence time of water (day)	97
Catchment characteristics	
Total catchment area (ha)	86.2
Arable land (ha)	33.9
Permanent pastures (ha)	42.5
Slope (%)	5.09

Table 2. Selected physicochemical properties of the studied pesticides

	Herbicides					Fungicides	
	Clethodim	Clopyralid	Fluroxypyr	MCPA	Prosulfocarb	Boscalid	Propiconazol
Physicochemical properties ^a							
Distribution							
Vapor pressure at 25 °C (Pa)	2.1×10 ⁻⁶	1.4×10 ⁻³	3.8×10 ⁻⁹	4×10 ⁻⁴	7.9×10 ⁻⁴	7.2×10 ⁻⁷	5.6×10 ⁻⁵
Henry's law constant, K _H	2.68×10 ⁻¹⁰	1.46×10 ⁻⁸	4.7×10 ⁻²	1.1×10 ⁻⁸	5.38×10 ⁻⁵	2.12×10 ⁻⁸	1.70×10 ⁻⁷
Solubility at 20 °C, pH 7 (mg/L)	5,450	143,000	6,500	29,390	13	5	150
pKa (25 °C)	4.47	2.01	2.94	3.73	–	–	1.09
Acid/base characteristic	Weak acid	Strong acid	Strong acid	Weak	No	No	Very weak
Major compound at pond pH	A ⁻ (L ⁺)	A ⁻ (L ⁺)	A ⁻ (L ⁺)	A ⁻ (L ⁺)	–	–	BH ⁺ (L ⁻)
K _{oc} ^b (mL/g)	23 ^c	5	68 ^c	74	1,693 ^c	772 ^c	1,086
K _d ^d (mL/g)	0.39	0.071	1.20	0.94	23.1	12.6	33.7
Persistence							
DT ₅₀ soil ^e (days)	3	11	51	25	10	118	214
Aqueous photolysis DT ₅₀ at pH 7 ^f	5	271	Stable	0.05	Stable	30	Stable
Aqueous hydrolysis DT ₅₀ at pH 7 ^f	Stable	Stable	223	Stable	Stable	Stable	53.5
Water–sediment DT ₅₀ ^g (days)	17		35	17	214	–	636

A acid, A⁻ conjugate base (acid that has lost a proton), B base, BH⁺ conjugate acid (base that has gained a proton), L ligand, L⁺ /L⁻ charge of the ligand

^aData obtained from the Pesticide Properties Database (PPDB) developed by the Agriculture and Environmental Research Unit (AERU) at the University of Hertfordshire (2014)

^b Organic carbon sorption coefficient

^cFreundlich adsorption coefficient to organic carbon

^d Particle/water partitioning coefficient

^e Half-life for field soil

^f In water phases

^g Sediment

Table 3. Hydrochemical parameters measured upstream (inflow) and downstream (outflow) from the fishpond

Water physicochemical parameters

	Inflow	Outflow
Temperature (°C)	11.6±4.8 (3.8–20.3)	12.8±6.0 (4.2–23.6)
Dissolved oxygen (mg/L)	8.6±1.7 (5.3–12.7)	7.4±0.0 (1.7–11.4)
Electrical conductivity (µS/cm)	1,090±192 (660–1,391)	748±297 (412–1,562)
pH	7.8±0.4 (7.0–8.4)	7.7±0.4 (7.2–8.4)
Total suspended solids (mg/L)	70.4±87.9 (5.1–441.0)	42.9±76.4 (4.7–364.3)
Volatile suspended solids (mg/L)	9.5±10.0 (0.8–46.7)	6.4±7.7 (1.4–38.5)

Table 4. Estimation of annual pesticide loads at the upstream and downstream locations and removal rates

Pesticide removal efficiency

Compound name	Catchment		Inflow	Outflow	Outlet load (g/year)	RL ^d (%)
	Application period	Applied amount (g) ^a	Inlet load ^b (g/year)	k _{outflow} ^c (day)		
Herbicide						
Clethodim	September	64	2.36–2.96	0.022±0.007**	1.14±0.43	33–76
Clopyralid	June	48	1.64–3.13	–		100
Fluroxypyr	June	96	7.25–12.61	0.006±0.005	0.94±1.39	–
MCPA	June	482	22.83–47.13	0.032±0.002***	0.75±0.13	96–99
Prosulfocarb	October	12,960	10.63–13.79	0.008±0.001***	14.69±1.99	0–8
Fungicide						
Boscalid	May	777	9.64–22.45	0.012±0.001***	1.60±0.26	81–94
Propiconazole	April	94	0.86–1.57	0.064±0.008***	0.36±0.01	57–78

^a Quantity of pesticides applied on the studied catchment^b Range (min–max) of estimated loads with Eq. 2 to Eq. 4^c First-order rate constants calculated with Eq. 5^d Load removal rate (RL) calculated with Eq. 1

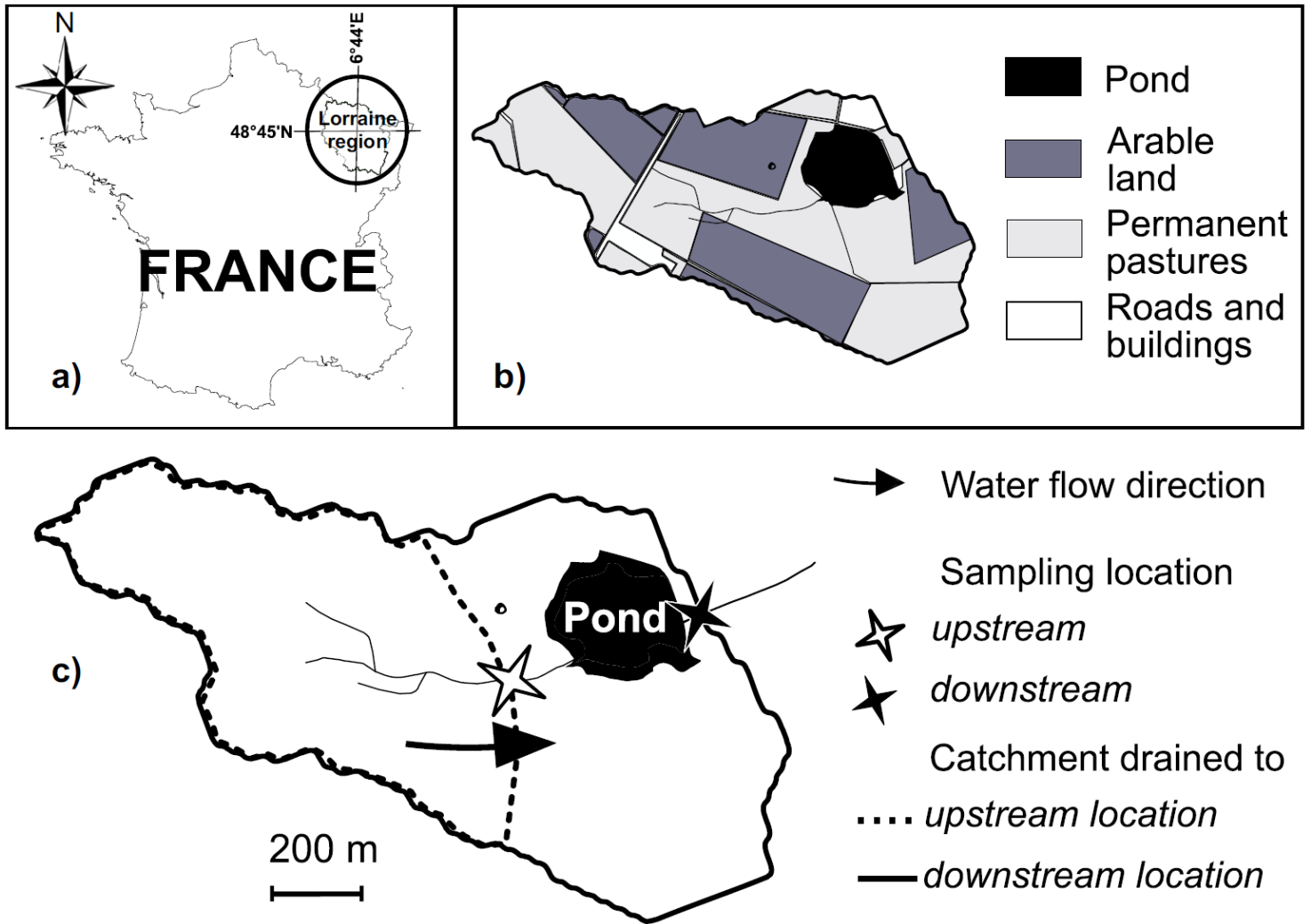


Figure 1. Studied fishpond and catchment: a location of the Lorraine Region in France, b catchment land cover characteristics, and c location of sampling stations

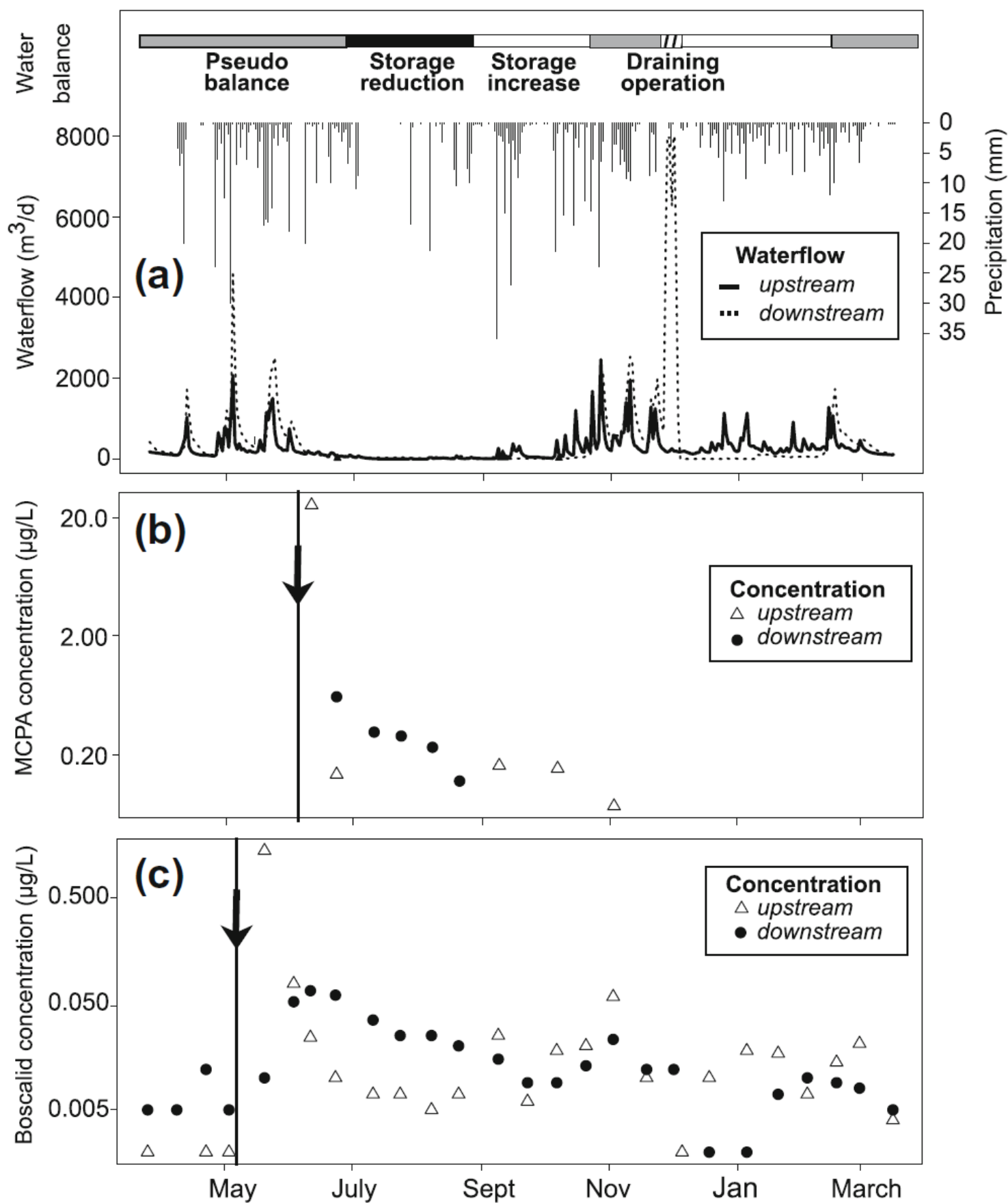


Figure 2. Time courses of a water discharges at the upstream and downstream location, b MCPA, and c boscalid concentrations. Arrows and vertical lines represent the time of application

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