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Barrage fishponds: Reduction of pesticide concentration peaks and associated risk of adverse ecological effects in headwater streams

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Keywords

Pesticide, toxic units, fish ponds, shallow lakes, headwater streams.

Abstract

Constructed wetlands have been suggested as pesticide risk mitigation measures. Yet, in many agricultural areas, ponds or shallow lakes are already present and may contribute to the control of non-point source contamination by pesticides. In order to test this hypothesis, we investigated the influence of extensively managed barrage fishponds (n = 1/4 3) on the dissolved concentrations of 100 pesticides in headwater streams over the course of a year. Among the 100 pesticides, 50 different substances were detected upstream and 48 downstream. Highest measured concentration upstream was 26.5 mg/L (2-methyl-4-chlorophenoxyacetic acid, MCPA) and 5.19 mg/L (isoproturon) downstream. Fishponds were found to reduce peak exposure levels as high pesticide concentrations (defined here as > 1 mg/L) generally decreased by more than 90% between upstream and downstream sampling sites. The measured concentrations in the investigated streams were compared to laboratory toxicity data for standard test organisms (algae, invertebrates and fish) using the toxic unit approach. When considering the threshold levels set by the European Union within the first tier risk assessment procedure for pesticide registration (commission regulation (EU) N° 546/2011), regulatory threshold exceedances were observed for 22 pesticides upstream from fishponds and for 9 pesticides downstream. Therefore, the investigated barrage fishponds contributed to the reduction of pesticide peak concentrations and potential risk of adverse effects for downstream ecosystems.

1. Introduction

Diffuse sources of pesticides used in agricultural areas are widely acknowledged as one of the greatest stressors to stream ecosystems in the European Union with more than 300 000 tons of active substances applied yearly (European Crop Protection Association, 2010; Verosmarty et al., 2010). Pesticide loss from agricultural catchments to water bodies occurs mainly through surface water runoff, flow through tile drains and spray-drift (Brown and Van Beinum, 2009; Kreuger, 1998; Ng and Clegg, 1997; Novak et al., 2003). In headwater streams (i.e., first or second order streams according to the Strahler classification) located in agricultural catchments, pesticide concentrations are subject to considerable and fast temporal variations due to strong connectivity with surrounding agricultural areas and limited dilution potential by other water sources (Garmouma et al., 1997; Leu et al., 2004; Meyer et al.,

2007; Rabiet et al., 2010). Because aquatic ecosystems contain species related to the target organisms of pesticides, undesirable side effects may occur in relation to high pesticide exposure (Liess and von der Ohe, 2005). The preservation of these headwater streams in terms of water quality is essential at the river basin scale considering that they make up most of the total river length and catchment area and that they are critical areas for pollutant dynamics as well as biodiversity support (Alexander et al., 2007; Gomi et al., 2002; Meyer et al., 2007).

To control the risks associated with pesticide occurrence in European surface waters, various pieces of legislation have been introduced (Brock et al., 2006). The Water Framework Directive (WFD) aims to maintain and improve the aquatic

environment in the European Union so that a “good ecological status” and a “good chemical status” are achieved (European Union, 2000). The chemical status depends on compliance with Environmental Quality Standards (EQS) for 45 so-called priority substances including 19 pesticides (European Union, 2008, 2013). These priority pesticides are currently being used or now banned, and represent potential problems in one or more European water basins (Brock et al., 2006). The European prospective procedure for the registration of pesticides, referred to as the Uniform Principles (UP), allows assessment of the risks posed by pesticides that are not regulated by the WFD (European Food Safety Authority, 2013; European Union, 2009, 2011). In the first tier of this risk assessment, environmental concentrations are compared to some threshold for adverse effects calculated from acute laboratory toxicity tests and the application of safety factors. Both pieces of legislation (WFD and UP) may be used to identify impaired headwaters that are candidates for the implementation of Best Management Practices to eliminate or minimize diffuse sources of pesticides (Stehle et al., 2011; Ensminger et al., 2013).

To limit surface water contamination, several measures have been suggested at the farm scale (e.g., active substance selection and substitution, proper use of pesticide spraying equipment), plot scale (e.g., conservation tillage) or catchment scale (e.g., grass buffer strips, riparian forest buffers, constructed wetlands) (Gregoire et al., 2009; Reichenberger et al., 2007). Constructed wetlands and vegetated ditches have been shown to be effective in reducing surface water contamination by pesticides in relation to high hydraulic retention time and plant coverage (Anbumozhi et al., 2005; Lacas et al., 2005; Locke et al., 2011; Matamoros and Salvadó, 2012; Stehle et al., 2011; Vallee et al., 2015; Vyzamal and Brezinová, 2015). Yet, in many agricultural areas, lentic waterbodies are already present with shallow lakes or ponds being the most common and widespread inland

water bodies (Downing et al., 2006). In France, it is estimated that shallow lakes cover 350 000 ha while lakes and reservoirs cover 100 000 ha (Bartout, 2015). However, the impact of ponds on pesticide contamination remains poorly understood. Among the lentic waterbodies already in place, barrage fishponds result from dam construction across valley streams and are, in many regions, located in headwater streams. Fishponds represent a large proportion of all surface waterbodies in France (1200 km²), the Czech Republic (410 km²) and Germany (420 km²) (Le Quere and Marcel, 1999; Pokorný and Hauser, 2002). They represent the main aquaculture systems for the production of fish and crustaceans worldwide with very diverse types (e.g., barrage, diversion or sunken ponds) and farming methods (i.e., from extensive to semi-intensive methods) (Anyusheva et al., 2012; Bostock et al., 2010; Coche et al., 1995).

Given the crucial role of headwater streams in determining downstream aquatic resources, knowledge of the ecosystem services and disservices provided by fishponds is essential to appropriate water resource management (Banas et al., 2002, 2008; Barszewski and Kaca, 2013; Broyer and Curtet, 2012; Lazartigues et al., 2012, 2013a, 2013b; Raczynska et al., 2012; Wezel et al., 2014). In a context of poor knowledge of regulating services provided by fishponds, some national agencies and environmental associations are calling for the destruction of barrage ponds in order to maintain ecological continuity (Blayac et al., 2014). To our knowledge, although pesticides are considered as a major stressor in agricultural headwaters, the influence of fishponds on this chemical stress has not been investigated yet. The present monitoring study applied the aforementioned regulatory protection goals to pesticide concentrations measured upstream and downstream from three barrage fishponds to allow for an assessment of the capacities and toxicological relevance of pesticide retention by these waterbodies (Elsaesser et al., 2011; Hunt et al., 2008; Stehle et al., 2011).

2. Material and Methods

2.1. Study area

The field campaigns were conducted in the Lorraine Region, north-eastern France (Fig. 1). The 30-year average annual air temperature in the study area was 10.7 °C with average minimum and maximum monthly temperatures of 2.2 °C in January and 19.7 °C in July, respectively. The average annual precipitation was 800 mm, well distributed over the year (30-year average, Château-Salins, Météo France, 2011). During the studied period (March 2013-March 2014), the cumulative precipitation was 946 mm with 29 rainfall events above 10 mm, including 17 events above 15 mm. At the gauging station managed by the DREAL Lorraine and located on the Seille River approximately 15 km downstream from the studied fishponds (Fig. 1), annual water flows calculated for the period 1986-2014 ranged between 45.106 m³/yr (2005) to 160.106 m³/yr (1986). The annual water flow during the investigated period was 126.106 m³/yr which is in the range of relatively wet years.

The Lorraine Region has a high density of fishponds which cover around 7000 ha and supply 1100 tons of fish yearly (Lorraine Regional Chamber for Agriculture, 2005; Le Quere

and Marcel, 1999). Barrage fishponds are commonly used for fish production and managed accordingly. Management operations include (i) drainage (during which all the water is discharged downstream in order to allow fish harvest) every one to three years in late autumn or early spring, (ii) filling up of the pond from tributaries and (iii) subsequent stocking when the pond is full. The hydrological cycles of fishponds are therefore largely controlled by water management rules set by the fishpond operators. The use of supplemental feeding or fertilizers in ponds is not common practice in the area and pesticides are not applied to ponds (Chary, 2013).

“Le pays des étangs” (literally “The land of the fishponds”) is an area with a high density of ponds, built on the Keuper Marls outcrops, located at the head of the Seille River catchment. On these hydric soils, agricultural drainage is often used to remove excess water and allow agricultural production. The area is characterized by three-year rapeseed (*Brassica napus* L.)-wheat (*Triticum aestivum* L.)-barley (*Hordeum vulgare* L.) sequences as well as fodder maize, large areas of pasture for livestock and extensive forests (Xiao et al., 2014). The typical spraying season for pesticides runs from March to November (Joulin et al., 2006).

2.2. Sampling sites and strategy

Three sites, named FP0, FP1 and FP2, were studied. Each site consisted of a fishpond and its catchment. They were located on the watershed of the Seille River and selected according to the following criteria: (i) major water inflow to the pond from a single tributary and (ii) water flowing in the streams throughout the year (although discharges were typically reduced to zero during the summer) and for the catchments (iii) different proportions of forest cover and agricultural land. The surface areas of the associated catchments (measured at the outlet of the fishponds) were respectively 63.9 ha, 345.3 ha and 86.2 ha (Table 1). The catchment of FP0 was mainly covered with forest (i.e., 64%). Agricultural land (permanent pastures and arable land) covered 34%, 82% and 88% of the catchments of FP0, FP1 and FP2, respectively (Fig. 1). Nominal water residence times (i.e., storage volume divided by mean daily outflow) were estimated at 37, 169 and 95 days, respectively (Table 1).

Sampling and measurement stations were installed on each of the three streams where the three selected barrage fishponds were located, by considering both upstream and downstream sectors (Fig. 1). Water samples were collected between March 2013 and March 2014 approximately twice a month. They were collected at the six stations using SIGMA SD-90 0 autosamplers programmed to obtain 24 hourly composite samples (hourly aliquots). Thereby, the measured concentrations represented the average concentrations which aquatic organisms can be exposed to over a 24-h period. Samples were retrieved within few hours after collection of the last sample, kept at 4 °C and processed within 48 h to avoid possible loss of compounds from the dissolved phase by sorption or degradation during sample storage. A total of 150 samples were analysed including 25 samples upstream and 25 samples downstream from FP0 (no water discharge at the end of August), 26 samples upstream and 22 samples downstream from FP1 (no water discharge downstream in November and December, when the fishpond is filling up subsequently to the draining operation for fish harvest) and 26 samples upstream and 26 samples downstream from FP2. Out of the 26 sample collection periods, 17 were rainy periods and 9 were dry periods.

2.3. Quantification of pesticides in water upstream and downstream from pond

The selection of the pesticides to be studied was based on expert knowledge regarding their use and occurrence in regional surface waters (pers. com. Moselle Chamber of Agriculture and Rhine-Meuse Water Agency) and technical feasibility to analyse them by LC-MS. A total of 74 herbicides, 19 fungicides, 3 insecticides, 2 plant growth regulators and 2 herbicide safeners were included (see Table S1 of the Supplementary Material section for the complete list). Pesticide concentrations were estimated in water as required by the European legislation (European Union, 2000, 2009).

The method used for detecting and identifying these 100 substances was based on liquid chromatography-electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) with multiple-reaction monitoring. Water samples were centrifuged before injection to eliminate the suspended solids. On-line

enrichment of the target compounds was performed on a Hypersil Gold column (20 mm x 2.1 mm i.d., with 12 mm particles) (Waters Corporation, Manchester, UK). For each sample, 1.4 mL was injected through this column. The loading run time was set to 2 min at a flow rate of 2 mL/min. Then, the analytes retained in the cartridge were progressively transferred to the chromatographic column with acidified water. 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 (150 x 2.1 mm i.d., with 1.7 mm 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% solution A and a 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 400 mL/min and the total run time was 18 min. Every sample was analysed in duplicate to check reproducibility. Recoveries were evaluated by spiking each sample at two concentration levels (limit of quantification and highest calibration point). Dilutions of heavily contaminated samples were performed (see Table S1 of the Supplementary Material section for the limits of quantification).

2.4. Data analysis

At each sampling station, the annual arithmetic mean and maximum concentrations were calculated for each pesticide reflecting the distinction made in the WFD between the Annual Average (AA-EQS) and the Maximum Allowable Concentration (MAC-EQS) Environmental Quality Standards (Lepper, 2005; European Union, 2000). Average and maximum values were also calculated for the sum of pesticide concentrations. For these calculations, non-detected substance was treated as zero and the concentrations of detected pesticides below the limit of quantification (LOQ) were set to half of their LOQ. For each fishpond, the reduction rate of maximum concentrations (%) was calculated as the relative decrease in maximum concentrations between downstream and upstream stations (Budd et al., 2009). The reduction rate of average pesticide concentrations was calculated in a similar way (i.e., downstream mean concentrations/upstream mean concentrations). To evaluate the toxicological relevance of the reduction in pesticide concentration mediated by barrage fishponds, risk estimates of adverse effects were compared between upstream and downstream locations as described below.

Assessment of the risk to organisms is always the combination of exposure and effect data (Table 2). In order to assess the risk of adverse effects associated with pesticide concentrations, the toxic unit (TU) approach was used (Sprague and Ramsay, 1965). The TU approach is based on comparison of pesticide concentrations with EC50 (effect concentration 50, i.e., the concentration which has an effect on 50% of the exposed organisms) and LC50 (lethal concentration 50, i.e., the concentration that is lethal for 50% of the exposed organisms) measured for a single substance on standard test species. In the present study, toxicity data for three groups of organisms (algae, *Daphnia* for invertebrates, fish) were collected from peer-reviewed literature (Belden et al., 2007; Chevre et al., 2005; Sch€afer et al., 2011) and

available databases (French Agency of Food, Environmental and Occupational Health and Safety, 2014; INERIS, 2012; Kegley et al., 2011; University of Hertfordshire, 2014; U.S. EPA, 2014) (see Table S2 of the Supplementary Material section for compilation of EC50 and LC50 for the selected species).

The potential toxicity of each individual pesticide to the three groups (algae, Daphnia, fish) was predicted in all water samples collected upstream and downstream from the studied fishponds. Individual TU values were calculated by dividing the measured concentrations of dissolved pesticides by the acute toxicity data for standard test organisms (Table S2, Supplementary Material). For a given water sample, the TU was calculated as follows:

$$TU_{i,sp} = C_i / TC_{i,sp}$$

where $TU_{i,sp}$ is the Toxic Unit for pesticide i and species sp , C_i is the concentration of pesticide i in the water sample and $TC_{i,sp}$ is the toxic concentration (i.e., EC50 for algae and Daphnia or LC50 for fish, compiled in Table S2, Supplementary Material) for pesticide i and species sp .

The potential toxicity of mixtures in a given sample was evaluated using the maximum TU (mTU) which is considered to be the highest of all the TUs previously calculated for a given sample. For a given sample, (mTU_{sp}) was calculated as follows:

$$mTU_{sp} = \max(TU_{i,sp})$$

Maximum TU was considered here as an indicator of the minimal expected toxicity of the sample. The sum of all TUs (sumTU) was not used because it could overestimate the toxicity of compounds with a dissimilar mode of action (Sch€afer et al., 2011). This choice led to neglect the potential additive, synergistic or antagonistic effects of pesticide mixtures but was guided by the fact that for 81% of the samples, the mTU_{algae} represented more than 50% of the sumTU_{algae}. As regards the risk for Daphnia or fish, mTU rep-

resented more than 50% of the sumTU in 65% and 69% of the samples, respectively.

The risk of adverse effects for aquatic organisms was evaluated by comparing TUs to the threshold of the European Uniform Principles (Commission Regulation N° 1107/2009 and 546/2011 of the European Union). In the framework of the European evaluation and authorisation of plant protection products, the first tier of pesticide risk assessment consists in comparing exposure estimates with a threshold for adverse effects (European Food Safety Authority, 2013; European Union, 2009, 2011). This protective threshold is calculated applying a safety factor to laboratory toxicity tests. Accordingly, the TU of a pesticide in water should not be higher than 0.1 when considering EC50 for algae and 0.01 when considering LC50 or EC50 for Daphnia and fish.

To compare the risk associated with pesticide occurrence in surface waters across sampling sites, different procedures can be used: (i) the deterministic risk assessment is performed by comparing a point estimate of exposure, usually the highest exposure incidence, to a threshold level (Jergentz et al., 2005; Vryzas et al., 2011); (ii) the probabilistic risk assessment provides estimates of the risk range and likelihood rather than a single point estimate (Solomon et al., 2000) or (iii) the relevance-driven risk assessment focuses on the frequency of threshold exceedances and given ecotoxicological relevance (TU levels) (Stehle et al., 2013). However, on the one hand, the deterministic risk assessment is performed by comparing a point estimate to a threshold level, while the full range of concentrations remains unconsidered. It appears therefore unsuitable for comparing sites with variable exposure patterns. On the other hand, the probabilistic risk assessment uses all data points to calculate threshold level exceedances and is therefore highly dependent on the amount of samples taken and on the sampling strategy when applied to field data. It may therefore be unsuitable for contaminants characterized by short term peak exposure patterns as observed in headwaters (Stehle et al., 2013). These different elements lead the relevance-driven risk assessment to be considered as the most suitable procedure in the present study. In order to conduct such an assessment, the frequency of TUs exceeding the UP criteria set by the European Union (i.e., 0.1 for algae, 0.01 for fish and Daphnia; European Union, 2009, 2011) and TU levels were documented and compared between upstream and downstream locations (Stehle et al., 2011, 2013).

3. Results and Discussion

3.1. Pesticide occurrence, concentrations and associated risk of toxicity upstream from fishponds

Water entering the fishponds (Fig. 1) was sampled 25-26 times at each upstream site. During the investigation period, among the 100 pesticides analysed (74 herbicides, 19 fungicides, 3 insecticides, 2 plant growth regulators and 2 herbicide safeners) in the 77 upstream samples, 50 different substances (38 herbicides, 11 fungicides and 1 insecticide) were detected at least once (see Table 3 and Table S3 for detailed results of detected substances). On average, a single water sample contained 11 pesticides including 8 herbicides,

3 fungicides and no insecticides. The herbicides frequently detected were mainly substances applied during the cultivation of cereals (isoproturon, chlortoluron, prosulfocarb, diflufenican and flufe-nacet), rapeseed (clethodim, clomazone, dimethachlor and meta-zachlor) or maize (bentazon and tritosulfuron). Three herbicides (isoproturon, chlortoluron and prosulfocarb) and one fungicide (boscalid) were detected in more than 50% of the samples collected upstream from the fishponds (Table 3). The higher relative proportion of herbicides compared to fungicides and insecticides was expected considering the number of herbicides analysed and is consistent with pesticide sales in the Lorraine Region (Joulin, 2006).

In the water samples collected upstream from the studied fishponds, the highest concentrations were measured for

herbicides with a maximum value for the highly water-soluble MCPA (26 µg/L in June upstream from FP2), while the highest fungicide concentration was measured for tebuconazole (1.8 µg/L in May upstream from FP2). Insecticides were detected occasionally but never quantified. Low insecticide concentrations may be explained by the fact that our sampling strategy focused on runoff events, while insecticide exposure patterns are mainly driven by spraydrift events (Stehle et al., 2013). Our results showing that herbicide concentrations were higher than those of insecticides or fungicides are consistent with data from small European streams available in peer reviewed literature (Kreuger, 1998; Berenzen et al., 2005). When considering indicators of central tendency, the median pesticide concentrations remained close to the detection limit due to the large number of concentrations below the limit of detection or quantification. The highest annual mean concentrations were measured for MCPA, dimethachlor, metolachlor and metazachlor which were the pesticides with the highest maximum concentrations (Table 3). These results reflect the general exposure patterns observed in small agricultural streams, i.e., incidences of transient peak concentrations while the baseline concentration remains close to the detection limit (Garmouma et al., 1997; Leu et al., 2004; Rabiet et al., 2010).

The WFD requires member states to compare monitoring data based on monthly grab samples to EQS to define the chemical status of surface waters (European Union, 2000). Of the six WFD priority substances monitored in the present study (aclonifen, atrazine, diuron, isoproturon, simazine and terbuthryn), three (aclonifen, simazine and terbuthryn) were never detected. Measured annual average and maximum concentrations of diuron and atrazine were below the AA-EQS and MAC-EQS, respectively. Only for isoproturon, maximum allowable concentrations were above the EQS of 1 µg/L in 2 samples collected upstream from FP2, while the annual average concentration remained less than the AA-EQS set to 0.3 µg/L. However, care should be taken when comparing concentrations measured in headwaters to the EQS as defined by the WFD. Indeed, the WFD primarily addresses relatively large waterbodies (water surface area >50 ha or catchment area >10 km²) where the exposure pattern is different from the short term peak incidences observed in agricultural streams (Lepper, 2005). Indeed, appropriate sampling strategies for the calculation of average concentrations in headwaters would be continuous time-proportional monitoring while maximum concentrations would be evaluated based on event sampling (Bundschuh et al., 2014). To evaluate the risk associated with pesticide occurrence in surface waters, the European UP seem more accurate as they focus on relatively small bodies of water in the direct vicinity of agricultural fields (Brock et al., 2006). The first tier of the UP focuses on maximum concentrations highlighting the relevance of peak concentrations in risk assessment (European Food Safety Authority, 2013).

When considering the UP criterion of the European Union for standard risk assessment (i.e., TU < 0.1 for algae, TU < 0.01 for fish and Daphnia; European Union, 2011), this regulatory threshold was exceeded at least once during the whole study period for five pesticides (among the 100 analysed). The highest annual risks of toxicity were found for algae upstream from FP2 and were due to the high concentrations observed for five herbicides (diflufenican, dimethachlor, flufenacet, metazachlor and metolachlor). For these five herbicides, TU_{algae} reached 3.38 (in November), 3.13 (in September),

0.67 (in November), 0.60 (in September), and 0.51 (in September), respectively. The high risk of toxicity associated with the lipophilic diflufenican (TU_{algae} = 3.38) was due to low acute EC₅₀ for green algae (0.25 µg/L) despite relatively low maximum concentrations (maximum of 0.8 µg/L). The high risk associated with the relatively soluble dimethachlor (TU_{algae} = 3.13) was a combination of relatively low EC₅₀ for algae (6.5 µg/L) and high maximum concentrations (maximum of 20 µg/L). The sensitivity of algae to herbicides used in agriculture has already been reported in headwater streams by Belden et al. (2007). Their study of 83 pesticides in 17 streams showed that median maximum TU values were 5-10-fold higher for primary producers than for Daphnia or fish species. In a study by Scheafer et al. (2011) in four of the five largest rivers of Germany, maximum TU values were significantly higher for insecticides (e.g., dichlorvos, pirimiphos-ethyl) when considering Daphnia magna.

When calculating the maximum TU, 14 water samples out of the 77 collected upstream exceeded the thresholds set by the European Union (i.e., TU_{algae} < 0.1, TU_{Daphnia} < 0.01 and TU_{fish} < 0.01; European Union, 2009, 2011). Although the UP criteria are regulatory thresholds for single substances, they should also be protective for pesticide mixtures (Bundschuh et al., 2014). The fact that we consider the maximum TU as the minimal expected toxicity of our samples suggests an underestimation of the ecotoxicological potential of pesticides in these streams (Scheafer et al., 2011).

3.2. Spatio-temporal variability of pesticide concentrations and associated risk of toxicity upstream from fishponds

The concentrations of pesticides in the upstream flows varied greatly depending on the investigated sites (Fig. 2). The lowest concentrations were measured in FP0, which is consistent with a catchment dominated by forest. Among the 100 considered substances, only two herbicides (i.e., dicamba and tritosulfuron) presented a specific profile for FP0 (Fig. 2, Table S3). The highest concentrations of pesticides were measured in the agricultural catchments of FP1 and FP2. For FP1, the maximum value for the sum of pesticide concentrations per sample was 8.6 µg/L with a maximum individual pesticide concentration of 8.3 µg/L for MCPA. For FP2, the sum of pesticide concentrations per sample reached a maximum of 41 µg/L with a maximum individual pesticide concentration of 26 µg/L for MCPA. The spatio-temporal variability of pesticide concentrations was indeed driven by a few herbicides (Fig. 2). The proportion of agricultural area and pesticide application rates were similar between FP1 and FP2 but measured concentrations were higher for FP2. Several hypotheses could explain the differences between FP1 and FP2, the most plausible being a dilution effect by a resurgence located upstream from FP1 or the reduction of the pesticide concentration by a small pond (1.1 ha surface area) located upstream from FP1 (31.6 ha surface area) (Fig. 1). It can be clearly seen from Fig. 2 that the highest risk was observed for FP2 (mTU up to 3.38), while the highest mTU measured in the other sites (FP0 and FP1) were much lower (maximum of 0.101, Table S4). High mTU were driven by high herbicide TU to algae (Fig. 2).

A strong temporal variation in the measured pesticide levels was observed. The herbicides with the highest concentrations changed over the months (Fig. 2, Table S3). Peaks of MCPA

and bentazon (applied on maize) were observed in May/June. Peaks of dimethachlor, metazachlor and metolachlor (applied on rapeseed) were observed in September and peaks of isoproturon (applied on cereals) were observed in November. As for fungicides, peaks of boscalid and tebuconazole (applied on rapeseed and cereals) were observed in May. The temporal variations in pesticide concentrations were correlated with the main time periods of agricultural pesticide application for rapeseed, barley and wheat which are May/June and August/September/October while the application time period for maize is May/June only (Joulin et al., 2006). Overall, there was a strong temporal pattern in pesticide occurrence in the small catchments studied due to homogeneity in dominant crops (i.e., cereals, rapeseed and maize) and short time periods favourable to pesticide application. The highest risk to algae was observed in FP1 during the month of May and in FP2, during the months of September, October and November.

Therefore, relatively high concentration peaks were measured for several herbicides and the risk of associated adverse effects could not be neglected in the agricultural headwater streams supplying the fishponds in FP1 and FP2. Reduction of the concentration peaks and of the risks of adverse effects in the downstream river is without a doubt desirable, especially during the spraying season for this class of pesticides. Fungicides and insecticides were detected at relatively low levels and the risk of adverse effects seems to be limited (Table S3).

3.3. Influence of barrage fishponds on pesticide occurrence and concentrations

The outflows of fishponds (Fig. 1) were sampled 22-26 times depending on the sites, as no sampling was done when there was no discharge (typically at the end of the summer, or during the filling of the pond following the draining operation). Among the 73 samples collected downstream from the fishponds, 48 different substances (35 herbicides, 11 fungicides and 2 insecticides) were detected at least once compared to 50 different substances upstream (see Table S3 of the Supplementary Material section for detailed results of detected substances). Four currently used pesticides (benoxacor, chloridazon, florasulam and quizalofop-p-ethyl) and one banned herbicides (monolinuron) were detected upstream but never downstream from the fishponds. Conversely, three substances (acetochlor, ametryn and carbofuran) were detected at the outlet of FP2; while they had not been detected in its tributary. These three pesticides are no longer authorized in France. These occurrences at the downstream sampling point could be explained by (i) the release under specific conditions (e.g., resuspension of bottom sediment) of pesticides previously retained into the waterbodies or (ii) the discharge of pesticides from agricultural plots adjacent to the pond (downstream from the upstream sampling point). Downstream from the fishpond, 8 pesticides (5 herbicides, 3 fungicides) were detected in more than 50% of the collected samples compared to 4 pesticides with detection frequencies above 50% upstream (Table S3). Overall, detection frequencies were similar or increased between upstream and downstream locations for 32 of the 53 detected substances. This result could indicate a higher and faster variation in pesticide concentrations upstream compared to downstream from the

ponds as observed for other pollutants (Banas et al., 2008; Del Guidice et al., 2014).

When considering individual pesticide concentrations and the sum of pesticide concentrations per sample, there was a clear trend in the reduction of maximum concentrations between the upstream and downstream stations for FP1 and FP2 (Fig. 2, Table 4). For the two fishponds located in agricultural catchments and highly exposed to pesticides, the maximum sum of pesticide concentrations per sample was reduced by a factor of 1.7-5.6 between the upstream and downstream stations. This trend was observed for herbicides and fungicides, while insecticides were at low concentrations. Among the twelve pesticides measured at concentrations greater than 1 mg/L either upstream or downstream from the fishponds (Table 4), isoproturon was the only one for which concentrations were greater downstream (5.19 mg/L) than upstream (1.38 mg/L) for FP2. Although maximum concentrations were generally lower at downstream sites than at upstream sites, it should be noted that for FP0 the highest concentrations, even if low, were observed downstream from the pond. As discussed previously, such higher concentrations at the downstream point could be explained by the release of pesticides from the fishpond or input areas adjacent to the fishpond.

When considering average values for both individual and sum of pesticide concentrations between upstream and downstream, a similar trend was observed. As the sampling strategy was not timeproportional, care should however be taken when interpreting the reduction in mean concentrations as a reduction in long term exposure. Stamer et al. (1995), while evaluating the influence of reservoirs on atrazine concentrations, observed a greater mean concentration at the outlet than in the unregulated upstream tributary even though the peak concentration in the tributary was more than four times lower than the peak concentrations in the reservoir outflow.

Pesticide concentration peaks, which represent a potential risk to aquatic life, were reduced by the implementation of the studied fishponds. Pesticide concentration reduction rates reported in constructed wetlands designed for the control of nonpoint source pesticide pollution are generally above 80% (Budd et al., 2009; Elsaesser et al., 2011; Matamoros et al., 2012; Passepport et al., 2013) which is comparable to the results obtained in the studied fishponds, although not purposely designed for the treatment of diffuse sources of pollution. Care should however be taken when comparing both systems. First, pesticide concentration reduction rates in constructed wetlands are generally calculated using inlet and outlet concentrations measured on the same day which has no sense in fishponds due to the duration (from weeks to months) and variation of hydraulic retention time. Indeed, heavy rainfall events and variation in soil conditions lead to a considerable increase in flow, especially in small headwater streams, and therefore varying hydraulic residence time, which complicates targeted sampling of corresponding upstream and downstream concentration peaks. Secondly, pesticide concentrations measured downstream may be the result of multiple inlets to the system while only the main tributary was measured.

Finally, the sampling strategy implemented (collection of 24 h-composite samples twice a month) has likely led to missing

some of the peak concentrations. 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 upstream. The sampling frequency implemented was therefore not sufficient to capture the true maximum concentration at the upstream sites. At the downstream sites, the variability of chemical concentrations was assumed to be strongly reduced in relation to the nominal residence times of the ponds (Banas et al., 2008; Del Giudice et al., 2014; Stoeckel et al., 2012; Vyzamal and Březinová, 2015). Therefore, the low sampling frequency was more adapted to capture the variability of chemical concentrations for the downstream sites. Assuming that the risk of missing pesticide peak concentrations was higher upstream than downstream due to low frequency sampling, the estimated reduction rate of the ponds are actually an underestimation.

3.4. Impact of fishponds on pesticide potential toxicity

When considering a very high risk for organisms corresponding to a TU threshold equal to one (i.e., the measured concentration equals the EC50 or LC50 value), two samples upstream from FP2 were above this value while none of the samples downstream from the fishponds presented such a potential toxicity. When considering the TU thresholds set by the European Union (i.e., $TU_{algae} < 0.1$; European Union, 2009, 2011), 14 samples and 22 individual pesticide concentrations exceeded this value upstream of the three studied ponds while 8 samples and 9 individual pesticide concentrations exceeded it downstream. In FP2, 14 samples were above the threshold upstream compared to 7 samples downstream. No samples were above the threshold upstream from FP1, whereas one sample was higher at the downstream point, due to the occurrence of a single herbicide (acetochlor). As previously discussed, possible explanations for the higher concentration and associated TU from FP1 include the release of pesticides from the fishpond under specific conditions or the discharge from adjacent agricultural plots, but unfortunately no element can help us to validate these hypotheses.

Overall, fishponds contributed to reduce peak pesticide exposure levels, which can reach potentially acute toxicity values for aquatic organisms in the upstream part of the catchment and consequently have adverse effects on the species present

4. Conclusion

Fish ponds located within watersheds exposed to pesticide, can buffer peak concentrations of pesticides in headwaters. The fishponds can thus reduce downstream risks and prevent some toxicity thresholds from being exceeded. Continued monitoring of these fishponds taking into account a wider range of stressors is needed to clearly determine spatial and

and potentially exposed to pulses of contaminants (Polard et al., 2011; Tlili et al., 2011). Previous studies have suggested that lentic waterbodies and their receiving streams may exhibit lower peak pesticide concentrations but longer periods of elevated concentrations than uninterrupted streams (Battaglin and Goolsby, 1998; Carleton, 2015; Stoeckel et al., 2012). Aquatic organisms upstream from the fishpond were therefore most likely to experience short pulses exposures whereas organisms immediately downstream from the fishpond were most likely to experience long term exposure to lower concentrations. It has been suggested that effects of pesticides may be similar when exposed for a short time to a greater concentration or for a longer time to a smaller concentration which would undermine the positive influence of fishponds on pesticide potential toxicity in streams (Belgers et al., 2011; Giesy and Graney, 1989). However, for certain pesticides, it has been demonstrated that in prolonged toxicity tests, a higher pulse exposure of a shorter duration may be more detrimental than an equivalent lower pulse exposure of a longer duration (Schulz and Liess, 2000; Tlili et al., 2011). The influence of the variation in pesticide exposure patterns between the waters upstream and downstream from fishponds on aquatic organisms should be further assessed.

In pesticide risk assessment, toxicity is usually based on exposure to one stressor. However, the results from this study confirm that multiple pesticides in agricultural streams are the norm. Although for many pesticides, TU values were below the UP criteria, little is known about toxicological interactions among multiple pesticides as it is impossible from a practical point of view to investigate all chemical combinations (Belden et al., 2007). Multiple stressors other than dissolved pesticides (e.g., particle-bound pesticides, metals, low dissolved oxygen, suspended matter, oxygen, habitat degradation, temperature) may also exhibit toxicological interactions and the influence of fishponds on this cocktail should be further investigated.

temporal variations in contaminant dynamics along headwater streams. This would allow mitigation measures to be more effective. The result of this research could be added to the "balance sheet" of ecosystem services and disservices provided by fishponds in head water streams. It could also provide the managers of river basins with insight into the implementation of best management practices.

Table 1. Summary of catchment and pond characteristics.

| Empty Cell | FP0 | FP1 | FP2 |
|---------------------------------------|--------|-------------------|-------------------|
| Catchment surface area (ha) | 63.9 | 345.3 | 86.2 |
| Dominant land use | forest | agricultural land | agricultural land |
| Pond surface area (ha) | 1.1 | 31.6 | 4.4 |
| Mean outflow rate (m ³ /d) | 493 | 3184 | 417 |
| Nominal residence time (d) | 37 | 178 | 95 |

Table 1. Risk assessment procedure for the evaluation of the toxicological relevance of pesticide retention by fishponds

| Steps | Description | Method |
|--------------------------------|--|--|
| Pesticide exposure | Concentrations of 100 pesticides upstream and downstream from 3 fishponds | Field monitoring |
| Pesticide effects | Collection of LC ₅₀ and EC ₅₀ from peer-reviewed literature for green algae <i>Pseudokirchneriella subcapitata</i> ; <i>Scenedesmus subspicatus</i> invertebrates <i>Daphnia magna</i> fish <i>Lepomis macrochirus</i> ; <i>Pimephales promelas</i> | Collection from peer reviewed literature 96 h duration – 50% reduction in growth and reproduction 48 h duration – 50% mortality or immobility 96 h duration – 50% mortality |
| Risk assessment and mitigation | Calculation of TUs for all pesticide concentrations Calculation of mTU (<i>i.e.</i> , maximum TU) for all collected samples Calculation of frequencies of regulatory threshold exceedance and ecotoxicological relevance for each sampling station | Toxic Unit (TU) approach Relevance-driven risk assessment |

Table 3. Frequencies of detection, limits of quantification, frequencies of quantification, mean and maximum concentrations, and maximum predicted toxicities for the most frequently detected pesticides (detection frequency > 10%) upstream from the three investigated fishponds.

| Upstream locations | | | | | | | |
|---------------------|------------------------|----------------------------|------------------------|--------------------------------------|-------------------------------------|--------------------------------------|--|
| Empty Cell | FD ^a (%) | LOQ ^b (µg/L) | FQ ^c (%) | Mean conc. ^d (µg/L) | Max conc. ^d (µg/L) | Max. TU _{i,sp} ^e | n° TU _{i,algae} >0.1 ^f |
| Herbicides | | | | | | | |
| Atrazine | 25 | 0.004 | 0 | 0.000 | 0.002 | 0.000 | 1 |
| Bentazon | 35 | 0.010 | 23 | 0.063 | 3.055 | 0.001 (<i>algae</i>) | |
| Chlortoluron | 57 | 0.004 | 52 | 0.024 | 0.395 | 0.003 (<i>algae</i>) | |
| Clethodim | 19 | 0.010 | 4 | 0.007 | 0.230 | 0.000 | |
| Clomazone | 25 | 0.004 | 19 | 0.032 | 1.675 | 0.000 | |
| Diflufenican | 36 | 0.010 | 18 | 0.023 | 0.846 | 3.384 (<i>algae</i>) | 12 |
| Dimethachlor | 42 | 0.004 | 22 | 0.335 | 20.350 | 3.131 (<i>algae</i>) | 3 |
| Dimethenamid-P | 43 | 0.004 | 35 | 0.021 | 0.401 | 0.024 (<i>algae</i>) | |
| Flufenacet | 42 | 0.004 | 29 | 0.054 | 3.020 | 0.665 (<i>algae</i>) | 1 |
| Fluroxypyr | 21 | 0.004 | 21 | 0.064 | 1.754 | 0.000 | |
| Flurtamone | 26 | 0.004 | 5 | 0.001 | 0.020 | 0.001 (<i>algae</i>) | |
| Isoproturon | 70 | 0.004 | 34 | 0.076 | 1.380 | 0.004 (<i>algae</i>) | |
| MCPA | 10 | 0.010 | 10 | 0.464 | 26.475 | 0.000 | |
| Mesosulfuron-methyl | 23 | 0.010 | 16 | 0.008 | 0.093 | 0.000 | |
| Metazachlor | 48 | 0.004 | 36 | 0.184 | 9.520 | 0.595 (<i>algae</i>) | 2 |
| Metolachlor | 38 | 0.004 | 26 | 0.217 | 5.140 | 0.514 (<i>algae</i>) | 4 |
| Metsulfuron-methyl | 30 | 0.004 | 23 | 0.005 | 0.101 | 0.001 (<i>algae</i>) | |
| Napropamide | 48 | 0.004 | 22 | 0.023 | 1.018 | 0.000 | |
| Propyzamide | 31 | 0.010 | 13 | 0.005 | 0.079 | 0.000 | |
| Prosulfocarb | 55 | 0.004 | 25 | 0.028 | 1.430 | 0.029 (<i>algae</i>) | |
| Tritosulfuron | 14 | 0.010 | 4 | 0.002 | 0.100 | 0.000 | |
| Fungicides | | | | | | | |
| Boscalid | 84 | 0.004 | 58 | 0.025 | 1.371 | 0.001 (<i>algae</i>) | |
| Carbendazim | 10 | 0.004 | 0 | 0.000 | 0.002 | 0.000 | |
| Cyproconazole | 22 | 0.004 | 6 | 0.001 | 0.043 | 0.000 | |
| Epoxyconazole | 49 | 0.004 | 23 | 0.008 | 0.336 | 0.000 | |
| Propiconazole | 39 | 0.004 | 10 | 0.002 | 0.088 | 0.000 | |
| Tebuconazole | 39 | 0.004 | 32 | 0.036 | 1.752 | 0.001 (<i>algae, Daphnia</i>) | |

a :FD: frequency of detection (>LOD).

b:LOQ: limit of quantification.

c:FQ: frequency of quantification (>LOQ).

d:For the calculation of mean and maximum concentrations, a non-detected substance was treated as 0 and a detected concentration below the limit of quantification (LOQ) was set to half of the LOQ.

e:Highest annual maximum toxic unit (mTU).

f:Number of annual mTU >0.1 for algae.

Table 1. Influence of fishponds on pesticide concentrations and potential toxicity measured in headwater streams.

| Empty Cell | FP1 | | | FP2 | | |
|---|-----------|------------|--------------------|-----------|------------|--------------------|
| | Upstream | Downstream | Reduction rate (%) | Upstream | Downstream | Reduction rate (%) |
| Pesticide concentration (average/maximum in µg/L) and reduction rate (average/maximum in %) ^a | | | | | | |
| Bentazon | 0.19/3.05 | 0.03/0.09 | 81/97 | | | |
| Boscalid | | | | 0.07/1.37 | 0.02/0.07 | 74/95 |
| Clomazone | | | | 0.09/1.67 | 0.01/0.03 | 92/98 |
| Dimethachlor | | | | 0.99/20.3 | 0.04/0.14 | 96/99 |
| Flufenacet | | | | 0.16/3.02 | 0.08/0.75 | 51/75 |
| Fluroxypyr | | | | 0.17/1.75 | 0.01/0.05 | 95/97 |
| Isoproturon | | | | 0.22/1.38 | 0.43/5.19 | -92/-276 |
| MCPA | 0.35/8.26 | 0.22/4.19 | 38/49 | 1.03/26.5 | 0.03/0.37 | 97/97 |
| Metazachlor | | | | 0.54/9.52 | 0.05/0.14 | 90/98 |
| Metolachlor | | | | 0.64/5.14 | 0.08/0.31 | 87/94 |
| Napropamide | | | | 0.07/1.02 | 0.00/0.03 | 94/97 |
| Prosulfocarb | | | | 0.08/1.43 | 0.04/0.54 | 48/62 |
| Tebuconazole | | | | 0.10/1.75 | 0.02/0.08 | 80/95 |
| Sum ^b | 0.67/8.62 | 0.40/5.17 | 40/40 | 4.61/41.2 | 1.04/7.38 | 77/82 |
| Maximum pesticide toxic unit (number of samples with $mTU_{algae} > 0.1$) ^c | | | | | | |
| Acetochlor | | 0.10 (1) | | | | |
| Diflufenican | | | | 3.38 (12) | 0.27 (7) | |
| Dimethachlor | | | | 3.13 (3) | 0.02 (0) | |
| Flufenacet | | | | 0.67 (1) | 0.17 (1) | |
| Metazachlor | | | | 0.59 (2) | 0.01 (0) | |
| Metolachlor | | | | 0.51 (4) | 0.03 (0) | |
| Maximum ^d | 0.02 (0) | 0.10 (1) | | 3.38 (14) | 0.27 (7) | |

a:Pesticide average and maximum concentration reduction rate calculated for pesticides measured at concentrations higher than 1 µg/L at least once at one of the upstream or downstream location. None of the concentrations measured for FP0 were above this threshold.

b:Sum of pesticide concentrations per sample (µg/L).

c:Pesticide TU reduction calculated for pesticides with a maximum $TU_{algae} > 0.1$. None of the TUs measured for FP0 were above this regulatory threshold (European Union, 2009, European Union, 2011).

d:Maximum toxic unit per sample.

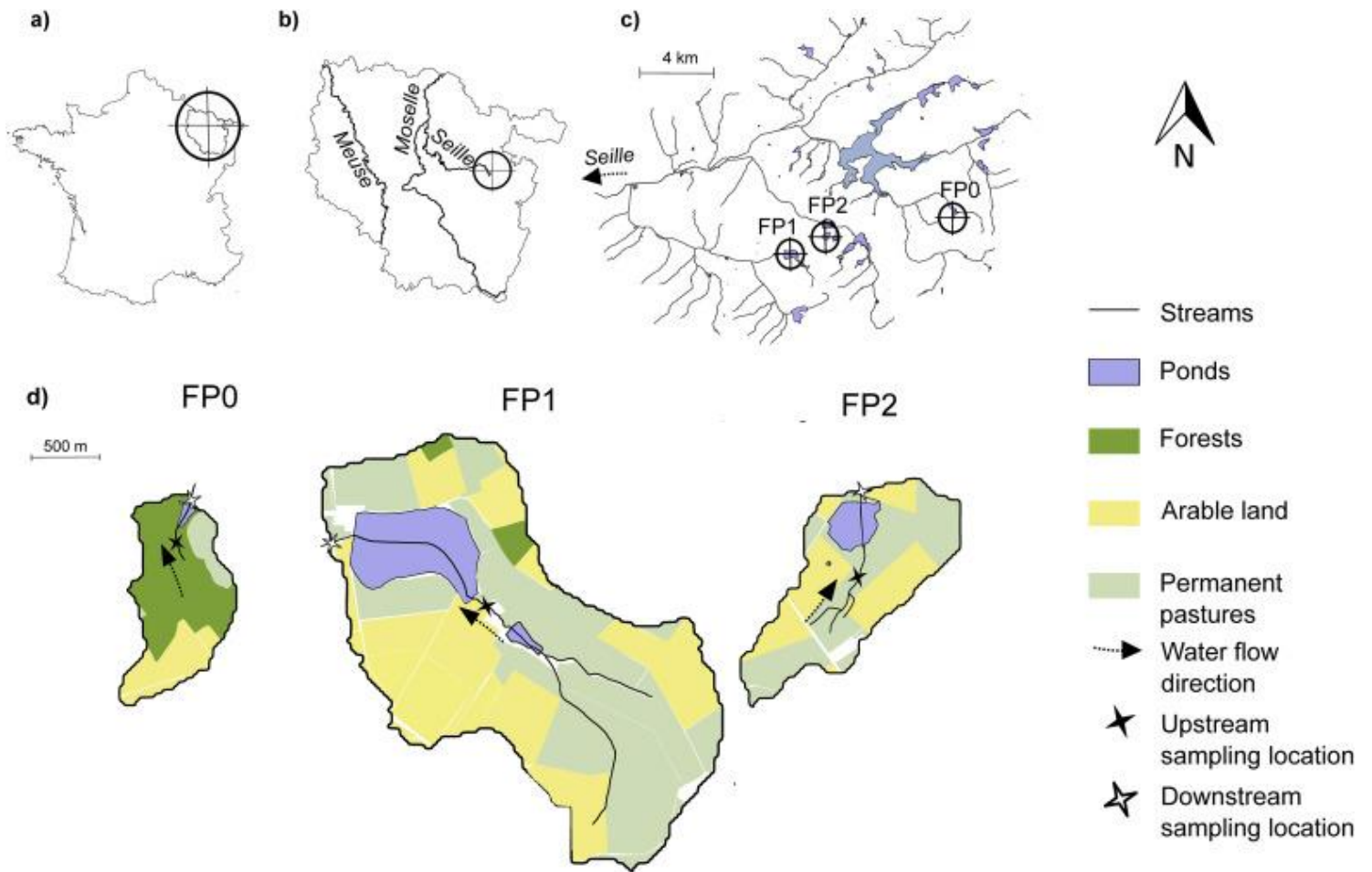


Figure 1. Location of the study areas

(a: France, b: Lorraine Region, c: Headwaters of the Seille River catchment) and land uses within the catchments with the sampling locations (d)

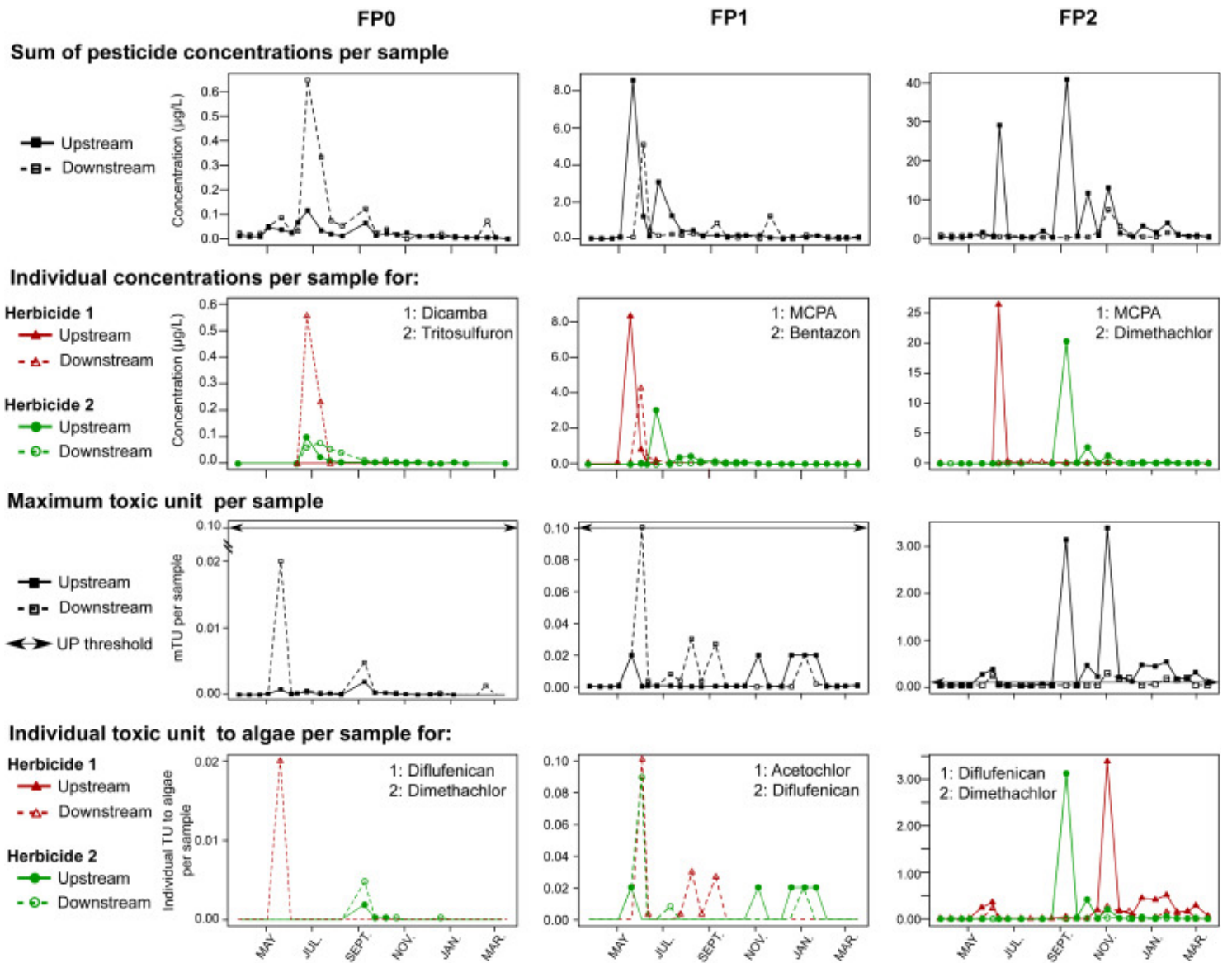


Figure 2. Presentation of spatial and seasonal trends of pesticide concentrations and predicted toxicities for the three studied sites (FP0, FP1, FP2).

Sum of pesticide concentrations per sample, individual concentrations (selection of pesticides with the highest concentrations), maximum toxic units (mTU) and individual toxic units (TU) to algae (selection of pesticides with the highest TU) are plotted for FP0, FP1 and FP2 at the upstream (continuous line) and downstream (dotted line) locations, as a function of time.

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