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Distribution of pesticides and some of their transformation products in a small lentic waterbody: Fish, water, and sediment contamination in an agricultural watershed

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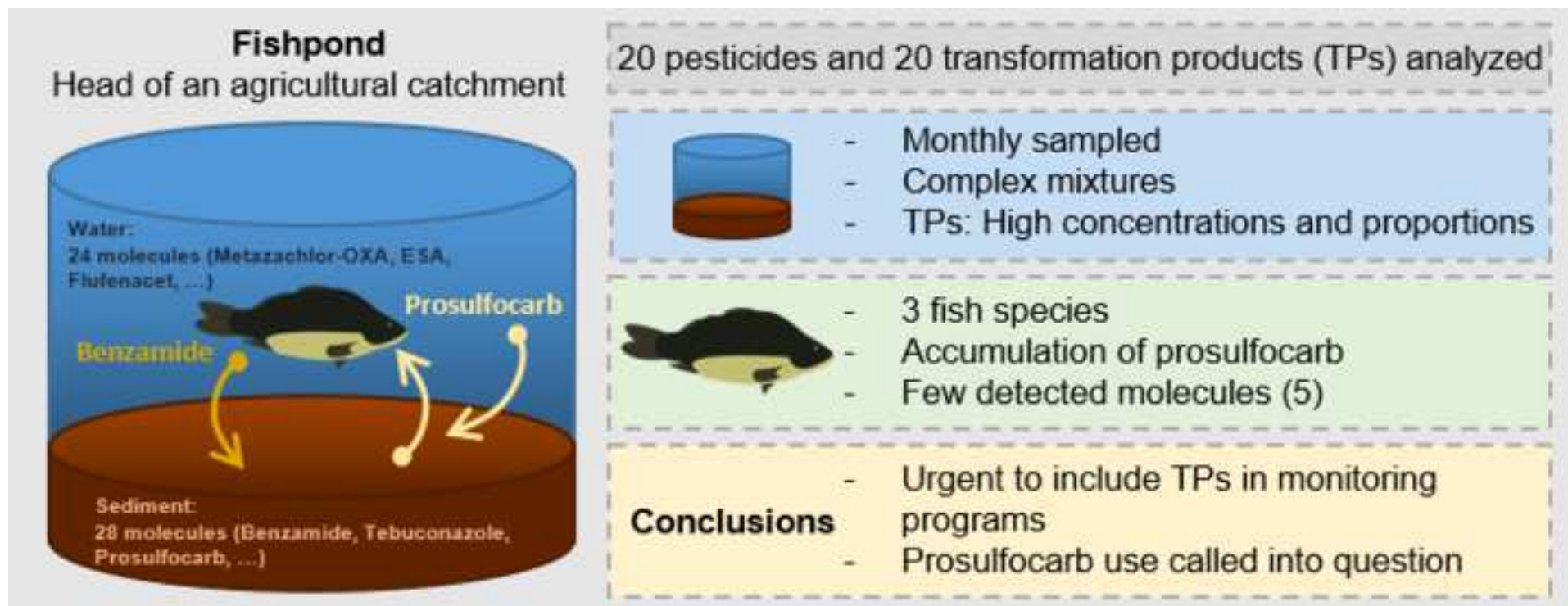
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### Highlights

- Pesticides (20) and transformation products (20, TPs) were analysed
- In abiotic matrices, complex mixtures and strong presence of TPs were observed
- Prosulfocarb significantly accumulated in three fish species
- Few contaminants were detected in fish samples
- TPs must be include in monitoring campaign to better assess environmental risks



## **Distribution of pesticides and some of their transformation products in a small lentic waterbody: Fish, water, and sediment contamination in an agricultural watershed**

### **Abstract**

More than 20 years after the Water Framework Directive was adopted, there are still major gaps in the sanitary status of small rivers and waterbodies at the head of basins. These small streams supply water to a large number of wetlands that support a rich biodiversity. Many of these waterbodies are fishponds whose production is destined for human consumption or for the restocking of other aquatic environments. However, these ecosystems are exposed to contaminants, including pesticides and their transformation products. This work aims to provide information on the distribution, diversity, and concentrations of agricultural contaminants in abiotic and biotic compartments from a fishpond located at the head of watersheds. A total of 20 pesticides and 20 transformation products were analyzed by HPLC-ESI-MS/MS in water and sediment sampled monthly throughout a fish production cycle, and in three fish species at the beginning and end of the cycle.

The highest mean concentrations were found for metazachlor-OXA ( $519.48 \pm 56.52$  ng.L<sup>-1</sup>) in water and benzamide ( $4.23 \pm 0.17$  ng.g<sup>-1</sup> dry wt.) in sediment. Up to 20 contaminants were detected per water sample and 26 per sediment sample. The transformation products of atrazine (banned in Europe since 2003 but still widely used in other parts of the world), flufenacet, imidacloprid (banned in France since 2018), metazachlor, and metolachlor were more concentrated than their parent compounds. Fewer contaminants were detected in fish and principally prosulfocarb accumulated in organisms during the cycle.

Our work brings innovative data on the contamination of small waterbodies located at the head of a basin. The transformation products with the highest frequency of occurrence and concentrations should be prioritized for further environmental monitoring studies, and specific toxicity thresholds should be defined. Few contaminants were found in fish, but the results challenge the widely use of prosulfocarb.

**Keywords:** Pesticides, Transformation products, Lentic waterbody, Fish, Bioaccumulation, Headwater streams

## 1. Introduction

Despite the fact that small waterbodies located at the head of basins are widespread and supply water to all downstream systems, they have long been ignored by researchers and public authorities. However, many of them are located in agricultural watersheds (Downing et al., 2006; Lorenz et al., 2017) where high amounts of chemicals are used to control pests and maintain high production levels. As a result, they may end up receiving large quantities of plant protection products (PPPs), but to date, there are few studies dealing with their occurrence and effects in small waterbodies (Lorenz et al., 2017). Among these aquatic ecosystems, fishponds are found in high density in several parts of the world, in fact they are the most commonly used type of facility for inland aquaculture (Banas et al., 2008; FAO, 2020). Exposure to PPPs in fishponds is likely to pose a risk not only to organisms and biodiversity (Gaillard et al., 2016a; Le Cor et al., 2021) but also to human consumers of fish (Brodeur et al., 2021; Lazartigues et al., 2013b). In fact, the accumulation of pesticides in fish has been proven by several studies (Brodeur et al., 2017; Clasen et al., 2018; Corcellas et al., 2015; Ernst et al., 2018; Jonsson et al., 2019; Oliveira et al., 2015; Pico et al., 2019; Reindl et al., 2015). In pond ecosystems, few works are available. However, we can notice that Brodeur et al. (2021) recently showed that the use of pesticides in arable areas near a fishpond caused toxicological damages, as well as the accumulation of atrazine up to  $105 \text{ ng.g}^{-1}$  and malathion up to  $23.7 \text{ ng.g}^{-1}$  in *Piaractus mesopotamicus*. In the same way, Lazartigues et al. (2013b) highlighted the accumulation of carbendazim up to  $0.34 \text{ ng.g}^{-1}$  of wet weight (wet wt.), metazachlor up to  $0.14 \text{ ng.g}^{-1}$  wet wt., and isoproturon up to  $0.85 \text{ ng.g}^{-1}$  wet wt. in *Cyprinus carpio*, *Rutilus rutilus*, and/or *Perca fluviatilis* reared in fishponds located at the top of agricultural watersheds. Contrary to expectations, not only hydrophobic

and non-polar contaminants (e.g. organochlorines, organophosphorus, pyrethroids) accumulate. For examples, atrazine (Brodeur et al., 2021, 2017; Ernst et al., 2018; Reindl et al., 2015), carbendazim (Ernst et al., 2018; Lazartigues et al., 2013b; Oliveira et al., 2015), metazachlor (Lazartigues et al., 2013b) can be found in fish tissues, while their log K<sub>ow</sub> are lesser than 3 (Kim et al., 2021). Thus, it appears of major importance to assess the occurrence and concentrations of polar PPPs not only in abiotic compartments of ponds but also in aquatic organisms, especially in fish which are in turn likely to contaminate consumers.

Moreover, once in the environment, PPPs can be degraded into transformation products (TPs) through abiotic processes, such as hydrolysis or photolysis (Speight, 2018a, 2018b), and biotic influences, such as microorganism degradation (Fritsche and Hofrichter, 2008; Katagi, 2013) or metabolism (Gerba, 2019). These various transformation pathways are likely to lead to the contamination of waters by mixtures of PPPs and TPs. Indeed, by analyzing data from 4,532 sites located in France, Germany, the Netherlands, and the United States, Schreiner et al. (2016) pointed out that the mixtures of two to five compounds, mainly composed of herbicides and TPs, were usually detected in streams. However, the number of compounds can be much higher, as shown by a wide-scope screening (500 molecules) conducted in the Júcar River Basin District in Spain, which revealed up to 18 compounds in one sample of surface water (Fonseca et al., 2019). Despite these findings, TPs are still poorly assessed in the environment (Schreiner et al., 2016), especially in rivers and small lentic waterbodies located in headwater streams.

The present study aimed to bring new data on the distribution of contaminants resulting from agricultural activities in a fishpond located at the head of an agricultural watershed where atrazine had been banned for nearly 20 years, but which remained



exposed to its TPs and to a wide range of other PPPs. In order to fulfill this objective, environmental monitoring of 20 PPPs and 20 TPs was conducted during a complete fishpond production cycle to measure concentrations of contaminants in water, sediment, and three fish species including *C. carpio*, which is the world's third most commonly produced fish in aquaculture (FAO, 2020). Results will allow for improved assessment of the distribution of PPPs between abiotic and biotic compartments and the proportions and persistence of their TPs.

## 2. Materials and methods

### 2.1. Study site

The study site is a fishpond (15<sup>th</sup> century) located in the Grand Est region in north-eastern France (GPS coordinates: 48°45'18.0"N 6°44'17.9"E). It is located on a headwater stream in a catchment (81 ha) dominated by arable lands (42%) and pastures (49%). The crops grown in the catchment are common in the region and mainly composed of wheat, barley, sunflower, rapeseed, and silage corn. The list of PPPs which have been recently used on the watershed is given in supplementary information (data obtained through personal interview of the farmer in 2014 and 2019, Table A.1 modified from Gaillard et al., 2016b and Le Cor et al., 2021). Principally, herbicides were the most widely used type of PPPs, and the local application rate is known to be higher than those of the regional average (Gaillard et al., 2016b). Dominant soil types are acidic Luvisol and gleyic Cambisol (Brethes, 1976; Gaillard et al., 2016b). The waterbody is surrounded by at least 5 m of vegetated buffer strips. The fishpond covers an area of 4.4 ha with a mean depth of 0.9 m (maximum of 2.2 m). The mean water residence time is 97 d (Gaillard et al., 2016b). Regarding physicochemical characteristics, the water pH ranges from 7 to 9,

the dissolved oxygen from 5 to 12 mg.L<sup>-1</sup>, and the conductivity from 650 to 1400 µS.cm<sup>-1</sup> according to the season (Le Cor, 2021).

The fishpond is managed in a traditional extensive way. No food is supplied, and fish consume the food that is naturally found in the pond (e.g. organic matter, zooplankton, invertebrates). The production (i.e. *C. carpio*, *R. rutilus*, *Scardinius erythrophthalmus*, *Tinca tinca*) is around 125 kg.ha.y<sup>-1</sup> (information relayed from fish farmers). In the Grand Est region, the production cycle consists of the following steps (Gaillard et al., 2016b). The pond is drained once every 1-2 years in winter making possible to bring the fish back to the dam and to harvest them using nets. Then, the pond is filled with water through its tributary, runoff, and precipitation. Usually, it takes approximately two months according to the environmental conditions to obtain a pond full of water. Finally, the pond is stocked with fish allowed to grow for the rest of the year. Fish are not caged and can move freely into the pond to find food occurring naturally in water or in sediment. The fish production can be either consumed, sold, and be introduced in other ponds in order to feed carnivorous fish, or sold to fishing associations to meet the demands of anglers.

In 2019, the fish stocking was done on March 27 (T0) and the fishing took place on December 3 (TF). During this period, the average monthly rainfall was 59.7 mm with a maximum of 116.4 mm in October and the average temperature was 13.1 °C with a maximum of 37.6 °C in July (Infoclimat, 2019).

## 2.2. Sampling design

### 2.2.1. Abiotic matrices

Water and sediment were sampled from March to November 2019. Three sampling zones were defined inside the fishpond to be representative of the entire waterbody (Banas, 2001): near the tributary, in the middle of the pond, near the dam/spillway. Every month and at each zone, four samples were collected and combined for each abiotic compartment, in order to obtain three final samples per month of water and three of sediment which will be subsequently analyzed. Water and sediment were collected using a polyethylene bottle (1 L) and a standard Ekman grab, respectively. After homogenizing the sediment samples and removing coarse particles such as rocks and leaves, 250 mL aliquots were placed in polyethylene vials. Water and sediment were stored at -18 °C. The 2019 summer drought prevented water or sediment sampling in the upstream zone in October. Thus, 26 water samples and 26 sediment samples were obtained for analysis.

### **2.2.2. Biotic matrix**

Fish were sampled at T0 and TF. They were approximately 1 year old at T0. Three species were selected for their representativeness of European production as well as their ecological differences: *C. carpio* (carp), *S. erythrophthalmus* (rudd), and *T. tinca* (tench). Both *C. carpio* and *T. tinca* are benthic organisms feeding primarily on invertebrates, detritus, and vegetal material found in sediment, while *S. erythrophthalmus* is a pelagic fish that feeds on invertebrate and macrophytes (Froese and Pauly, 2021). According to conventional fish farming practices, all fish coming from several ponds, were introduced at the same time into the pond. At T0, 14 *C. carpio*, 9 *S. erythrophthalmus*, and 6 *T. tinca* were sampled among the fish to be subsequently introduced into the pond. At TF, 17 *C. carpio*, 9 *S. erythrophthalmus*, and 7 *T. tinca* were sampled. All individuals were randomly

sampled and provided by the fishpond owner. Mean weights ( $\pm$  SEM) of each species at T0 and TF are given in supplementary information (Table A.2). In France, the consumption of freshwater fish is low in contrary to other parts of the world (FAO, 2020). These fish are mainly intended either to be reintroduced into other ponds or rivers to satisfy the demand of anglers, or will be used as forage fish by fish farmers to allow the growth of carnivorous fish (e.g. *Esox lucius*, *P. fluviatilis*). However, in some areas of France, carp can be consumed (usually at a slightly larger size than that collected at TF during our study). Contaminant concentrations were assessed in the entire body of all three species. For *C. carpio*, since this species is largely used for human consumption all over the world (FAO, 2020), the fillets was analyzed separately. For this purpose, bigger individuals were selected to better match the dietary habits. Then dorsal and ventral muscles were extracted from 7 and 8 individuals at T0 and TF, respectively ( $45.4 \pm 7.6$  g). All samples were stored at  $-18$  °C.

## 2.3. Contaminant analysis

### 2.3.1. Standards and reagents

We used ultrapure water from Biosolve-chemicals (Dieuze, FR) and Fisher Chemical (Geel, BE), acetonitrile (ACN,  $>99.9\%$  grade of purity) from Biosolve-chemicals (Dieuze, FR) and Honeywell (Seelze, DE), heptane from Merck (Darmstadt, DE), and formic acid, methanol and isopropanol from Biosolve-chemicals (Dieuze, FR). All were of LC-MS quality. Magnesium sulfate was purchased from Sigma-Aldrich (Saint-Louis, MO, USA).

Analytical standards were of >95% grade of purity. Individual solutions prepared in ACN (100 mg.L<sup>-1</sup>) were stored at -18 °C and mixed before analysis to obtain a concentration of 5 µg.L<sup>-1</sup>. They were purchased from A2S (Martignas-sur-Jalle, FR), Cambridge Isotope Laboratories (Tewksbury, MA, USA), Dr. Erhenstorfer (Ausburg, DE), Honeywell (Seelze, DE), HPC standards GmbH (Cunnersdorf, DE), Neochema (Bodenheim, DE), and Toronto Research Chemicals (North York, CA).

### **2.3.1. Sample treatments**

#### **2.3.1.1. Water**

For each sample, 1 mL aliquots of water were transferred into polypropylene centrifuge tubes, mixed with 10 µL of internal standard solution (individual concentration range of 50-250 ng.L<sup>-1</sup>), and vortexed for 10 s. Tubes were centrifuged (5810R, Eppendorf, Montesson, FR) at 20,800 g and 18 °C for 10 min to separate suspended particles. Afterwards, the supernatants were transferred into 2 mL glass vials before being directly injected into high-performance liquid chromatography-electrospray ionization-tandem mass spectrometry (HPLC-ESI-MS/MS).

#### **2.3.1.2. Sediment**

Sediment samples were freeze-dried for 92 h, sieved at 2 mm, and ground up using an agate pestle. For each sample, 0.5 ± 0.01 g was weighted. An internal standard solution (10 µL, individual concentration range of 50-250 ng.L<sup>-1</sup>) was added and the solvent (ACN) was evaporated under a fume hood for 10 min. Falcon tubes were filled with a 5 mL mixture of ACN and LC-MS quality water (90:10), vortexed for 10 s, and centrifuged (3,200 g, 15 min, 18 °C). The supernatants were transferred into

glass test tubes and placed under a gentle nitrogen stream at 30 °C to evaporate solvents (Multivap 54, LabTech, Sorisole, IT). Next, 500 µL of acidified water (0.1% formic acid) was added. The tubes were vortexed for 10 s. Then, the solution was transferred into polypropylene centrifuge tubes using a Hamilton syringe. The final volume was adjusted to 1 mL with formic acid (0.1%). Samples were centrifuged (20,800 g, 10 min, 18 °C) and the supernatants were transferred into 2 mL glass vials **prior being injected into the HPLC-ESI-MS/MS.**

### **2.3.1.3. Fish**

The extraction protocol was based on a QuEChERS-type solid-liquid extraction with low temperature partitioning previously performed on waterfowl eggs (Dufour et al., 2020). Samples were freeze-dried for 92 h, ground, and filtered using a 2 mm mesh size sieve. On average ( $\pm$  SEM), the water loss after freeze-drying was  $78.33 \pm 0.52\%$  for *C. carpio* whole body,  $83.6 \pm 0.95\%$  for *C. carpio* fillet,  $76.57 \pm 1.75\%$  for *S. erythrophthalmus* whole body, and  $79.29 \pm 0.25\%$  for *T. tinca* whole body. Then, 0.03 g of matrix was weighted in a polypropylene centrifuge tube. A volume of 0.5 mL of LC–MS quality water was added, and the sample was mixed using Geno/Grinder (SamplePrep 2010 Geno/Grinder, SPEX, Costa Mesa, CA, USA) at 16 Hz for 10 min. One milliliter of acidified ACN (0.2% of formic acid) and 0.5 mL of heptane were added, before mixing with Geno/Grinder (16 Hz, 10 min). After centrifugation (9,500 g, 10 min, 20 °C, SIGMA 3K3OH, Fisher, Osterode am Harz, DE), the supernatant was discarded and 0.6 ml of the remaining solution was transferred into a polypropylene centrifuge tube containing 0.3-0.32 g of magnesium sulfate and three zirconium oxide grinding balls (3 mm, Fisher Scientific, Illkirch, FR). The new solution was mixed using Geno/Grinder (16 Hz, 10 min) and centrifuged (9,500 g, 2 min, 20

°C). Ultimately, 0.15 mL of supernatant was transferred into a 2 mL chromatographic vial with a fixed 300 µL glass insert.

### 2.3.2. PPP and TP quantification

Forty compounds were analyzed (Table 1) in all samples. They were selected according to PPP use in the watershed since 2000 as well as substance occurrence in a complex matrix (sediment) of the fishpond (preliminary analysis, data not shown). Limits of detection (LODs) and quantification (LOQs) for each matrix are provided in table 1 (CAS Registry Numbers are given in table A.3). All samples were analyzed by HPLC-ESI-MS/MS. Detailed parameters are given in supplementary materials (Tables A.4-A.7).

For the abiotic samples, HPLC-LC20AD (Shimadzu, Marne-la-Vallée, FR) coupled with a QTRAP<sup>®</sup> 5500 system (Sciex, Villebon-sur-Yvette, FR) was used in both positive and negative modes (Tables A.4 & A.5). Quantification was performed with internal calibration. Analytes paired with internal standards for quantification are described in table A.4. The validation procedure of the method followed the French standard NF T90-210 (AFNOR, 2018). Blank samples (internal standard solution in LC-MS quality water) were included in each series to control the absence of contamination during the analytical process. Moreover, quality controls composed of a mix of the internal standard solution, analyzed molecules (in ACN), and acidified quality LC-MS water (0.1% formic acid) were placed at regular intervals (every ten samples) and at the end of each series. If the concentration exceeded ( $\pm 10\%$ ) the highest calibration point, it was diluted to meet the calibration rate. Recoveries, provided in table A.3, were controlled by spiking one sample per injection series. The LOQs were determined as the smallest tested concentration for which the inter-day

precision was lesser than 30% ( $LOD = LOQ/2$ ). Concentrations were adjusted if recoveries were not comprised between 80 and 120%. MultiQuant software (v. 3.0.1, Sciex, Villebon-sur-Yvette, FR) was used to interpret the data. Recoveries were null (no concentration assessment) for alachlor and flufenacet-OXA in sediment.

Concerning fish, compounds were matrix-matched quantified (linear regression) according to a recently published method (Dufour et al., 2021, 2020). HPLC-ESI-MS/MS was conducted using 1290 Infinity UPLC (Agilent Technologies, Massy, FR) coupled with QTRAP<sup>®</sup> 5500 in both positive and negative modes (Tables A.6 & A.7). All details on quality control are described in Dufour et al. (2021). In brief, *T. tinca* bred in controlled conditions in an experimental platform of aquaculture (URAFPA, University of Lorraine) were used as reference. Each sample was analyzed once, but positive extraction controls (spiked reference matrix) as well as negative controls (blanks without matrix and blanks of unspiked reference matrix) were systematically extracted for each extraction batch in order to control recoveries and to assess potential contamination during analysis. The LOQs were defined as the smallest tested concentration for which the inter-day precision was lesser than 30% ( $LOD = LOQ/3$ ). Determined concentrations were corrected when recoveries (provided in table A.3) fell outside the 80-120% range. The protocol was developed for fish samples following European guidance recommendation (European Commission DG-SANTE, 2019). Analyst software (v. 1.6.2, Sciex, Villebon-sur-Yvette, FR) was used to interpret the data.

Contamination was found in the reference matrix for fipronil, fipronil-sulfone, isoproturon, prosulfocarb, and metolachlor. Their LOQs were set at three times the quantified concentrations in blank samples, thus no LODs were defined.

For both abiotic and biotic matrices, the frequencies of detection (FODs) and



quantification (FOQs) of compounds were determined in each matrix. Mean concentrations in water and sediment were calculated by averaging the mean concentrations of monthly samples. As data below the LOQ should be treated and interpreted with caution (Hecht et al., 2018), and to avoid an averaging based on a large set of unquantified values, substitutions were made when FOQs > 90%: concentrations below LODs were estimated as null, and those comprised between LOD and LOQ were set to LOQ/2 (Gaillard et al., 2016a; Le Cor et al., 2021). In other cases (FOQ < 90%), mean concentrations were not calculated. Concentrations were expressed in  $\text{ng}\cdot\text{L}^{-1}$  in water, in  $\text{ng}\cdot\text{g}^{-1}$  of dry weight (dry wt.) in sediment, and in  $\text{ng}\cdot\text{g}^{-1}$  wet wt. in fish whole body and fillet. Conversion into  $\text{ng}\cdot\text{g}^{-1}$  wet wt. was obtained for each fish sample by applying individual water loss rates.

#### **2.4. Determination of the total lipid content**

Total lipid contents of all samples were determined with the aim to explain potential variations in concentrations between fish species/tissue and sampling times and to make this information available to readers who wish to compare it with other research studies (e.g. studies carried out on older and often more lipophilic pesticides for which this lipid content is essential). The method is based on the Folch's protocol (Folch et al., 1957; Roche et al., 2009). Briefly, 10 mL of Folch solution composed of chloroform and methanol (2:1 v/v) was added to 1 g of a freeze-dried sample, vortexed for 15 min, and filtered on fritted glass mounted under vacuum. An ASE tube was inserted into the vacuum flask to collect the filtrate after several rinsing cycles with a Folch solution (final volume of 30 mL). Then, the filtrate was transferred into a separation funnel with 8.8 mL of NaCl solution (0.73%) and agitated. After 2 h of decantation, the supernatant was discarded and the remaining solution containing

lipids and chloroform was collected into pre-weighed ASE tubes, placed under a nitrogen stream at 30 °C to evaporate solvents (Multivap 54, LabTech, Sorisole, IT), and lastly placed in an oven overnight to remove trace solvents. The total lipid content was obtained through gravimetric control. All samples were analyzed twice in order to control the accuracy of the method.

## 2.5. Statistical analysis

Regarding contaminant concentrations and lipid content measured in fish whole body and fillet, statistical differences between sampling times and species/tissue were assessed performing the Kruskal-Wallis rank sum test followed by Dunn's test of multiple comparisons using rank sums with the Holm correction. Substitutions of values <LODs and <LOQs were applied when needed according to the previously described method for statistical analysis purposes. All statistical analyses and graphical illustrations were carried out using R software (v. 4.0.0, © The R Foundation, 2020).

## 3. Results

### 3.1. Contaminant concentrations in water and sediment

The occurrence and concentrations of detected substances in water and/or sediment samples are presented in table 2. In both matrices, the highest maximum concentrations were measured for dimethenamid (1710 ng.L<sup>-1</sup>, FOQ = 22.2%) and for benzamide (5.44 ng.g<sup>-1</sup> dry wt., FOQ = 100%), respectively, and the highest mean concentrations (estimated only for compounds detected at least 90% of the time) were assessed for metazachlor-OXA (519 ± 57 ng.L<sup>-1</sup>, FOQ = 100%) and for

benzamide ( $4.2 \pm 0.2 \text{ ng.g}^{-1}$  dry wt., FOQ = 100%), respectively. Some TPs were found to show higher concentrations than their parent compounds (in both compartments: atrazine-2-hydroxy, dimethachlor-ESA, metazachlor-ESA and metazachlor-OXA; in water: flufenacet-ESA and flufenacet-OXA and metolachlor-ESA, metolachlor-OXA; in sediment: imidacloprid-desnitro and terbuthylazine-desethyl-2-hydroxy).

Over the whole study period, in water and sediment, respectively 24 (14 PPPs + 10 TPs) and 28 (14 PPPs + 14 TPs) compounds were detected (FOD > 0%) at least one time. All water and sediment samples were multi-contaminated. The water sample in which the greatest diversity of contaminants was found contained 20 different chemicals including 9 TPs in May, while it was found a maximum of 26 substances including 13 TPs for the sediment sample in May and November. In all samples, 10 substances (2 PPPs + 8 TPs) were always detected (FOD = 100%) in water and 14 (8 PPPs + 6 TPs) in sediment. Moreover, the contaminant mixtures in water and sediment were different. In fact, 4 compounds were only detected in water, and 9 only in sediment (Table 2). Substances that are not mentioned in table 2 were never detected in either of the matrices (16 substances among 40 in water and 10 substances among 38 in sediment)

## **3.2. Contaminant concentrations in fish**

### **3.2.1. Fish whole body**

Among the 40 analyzed substances, only benzamide, isoproturon-monodesmethyl, prosulfocarb, and tebuconazole were detected in at least one fish whole body sample. Benzamide was quantified in all whole body samples, except for S.

*erythrophthalmus* in which FOD and FOQ = 88.9%. For this TP, a decreasing trend was observed but the difference between T0 and TF was significant only for *T. tinca* ( $p$ -value < 0.01, Fig. 1). Concentrations of prosulfocarb assessed in whole body were significantly higher after fishpond exposure in all studied species ( $p$ -value < 0.05, Fig. 2). At TF, FOQ = 100% in all fish samples, while it was quantified at T0 in only 28.6% of *C. carpio* samples (FOD = 100%), 0% of *S. erythrophthalmus* samples (FOD = 88.9%), and 66.7% of *T. tinca* samples (FOD = 100%). For both molecules, no significant difference was found between species at T0 or at TF. Sporadically and only at TF, isoproturon-monodesmethyl was detected in 14.3% of *T. tinca* samples, but it was never quantified; tebuconazole was quantified in *S. erythrophthalmus* (FOD and FOQ = 22.2%, maximum concentration = 0.94 ng.g<sup>-1</sup> wet wt.) and in *T. tinca* (FOD and FOQ = 14.3%, maximum concentration = 0.27 ng.g<sup>-1</sup> wet wt.). None of the *T. tinca* were contaminated simultaneously with both isoproturon-monodesmethyl and tebuconazole.

### 3.2.2. Fish fillet

Only 4 compounds among the 40 analytes (benzamide, imidacloprid-desnitro, isoproturon-monodesmethyl, and prosulfocarb) were detected in at least one fish fillet sample. The same trends were observed in the fillet and whole body of *C. carpio*. The concentration of benzamide decreased, while that of prosulfocarb increased between T0 and TF (not significant, Fig. 1 & 2). Both molecules were always quantified, except prosulfocarb at T0 (FOD = 100% and FOQ = 28.6%). Although fillet samples seemed to be less contaminated than whole body samples with benzamide and prosulfocarb, no significant difference was observed between them at each sampling time (Fig. 2). Finally, at TF, isoproturon-monodesmethyl was

detected in 37.5% of fish fillet samples (FOQ = 0%), and imidacloprid-desnitro was detected and quantified in 12.5% of them (maximum concentration = 0.64 ng.g<sup>-1</sup> wet wt.).

### 3.3. Lipid content in fish samples

The results for the lipid content of fish samples are given in supplementary information in table A.8. They mostly showed significant differences between *C. carpio* whole body and fillet at TF ( $p$ -value < 0.01). No significant differences were found between T0 and TF for any of the analyzed species/tissues.

## 4. Discussion

### 4.1. Water and sediment compartments

The sampling site was a dam pond supporting fish production. Like most fishponds around the world, it is located in an agricultural area at the beginning of the hydrographic network (Downing et al., 2006; Lorenz et al., 2017). Its catchment is characterized by an intensive agriculture, frequently practiced in France and in other parts of the world, in which several PPPs are used. PPPs found in samples were applied on crops located on the catchment during the last 10 years (Tables 2 & A.1), except bentazone, chlorotoluron, imidacloprid which is forbidden since 2018 in France (Legifrance, 2018), metolachlor, and terbuthylazine according to our knowledge. Nevertheless, these compounds may have been used before 2010 or after without our knowledge, as all of them could be applied on type of crops found in the catchment such as wheat or silage corn.

The fishpond received the entire water flow, and thus all transported suspended solids. A recent work by Le Cor et al (2021) has shown that the tributaries that supply water to our study pond can carry numerous PPPs or TPs. These authors observed more pronounced inputs during the winter but also after the first spring rains. Thus, the fish that are in the pond in the spring, but also the organisms that will reproduce and develop during this period, are likely to be subject to the potential deleterious effects of the pesticides that have entered the pond and are contained in the water and sediments, and may even be transferred into the trophic chains.

Depending on their properties (e.g. log  $K_{ow}$ , polarity, ionization), molecules can be sorbed to sediment particles (Piwoni and Keeley, 1990). Hydrophobic compounds are particularly affected. Some properties of the surrounding environment (e.g. pH, temperature, organic carbon content in sediment, particle size) also modulate sorption efficacy (Gao et al., 1998; Piwoni and Keeley, 1990). For this reason, mixture compositions were dissimilar between water and sediment compartments. For instance, 3,5,6-trichloro-2-pyridinol, metolachlor, flufenacet, and prosulfocarb, (log  $K_{ow}$  values > 3, [Table A.8](#), Kim et al., 2021), were found in greater proportion in sediment than in water (Table 2). This demonstrates the relevance of searching for contaminants in both compartments to better assess the chemical quality of waterbodies.

A previous study conducted by Lazartigues et al. (2013b) in 2008/2009 assessed the contamination of water and sediment from the same fishpond as the one studied. A strong decrease in concentration peaks for isoproturon and metazachlore was observed (2,690 and 410 ng.L<sup>-1</sup> in water, respectively, in Lazartigues et al., 2013b). This probably indicates a better environmental quality induced by changes in agricultural practices, as isoproturon-based pesticides are banned since 2016 in the

European Union (European Commission, 2016), and as metazachlor was not applied to the arable lands of the watershed (personal communication of the landowner). Concerning dimethachlor, our results underline the importance to obtain LOQ as low as possible. In fact, it was not detected in water in Lazard et al. (2013b), but it was found in a few samples (max: 7.95 ng.L<sup>-1</sup>, Table 2) with a LOQ two times lower (5 ng.L<sup>-1</sup>, Table 1).

Several TPs were quantified at higher concentrations than their parent compounds, such as dimethachlor-ESA, metazachlor-ESA and metazachlor-OXA in both matrices, metolachlor-ESA, metolachlor-OXA, flufenacet-ESA and flufenacet-OXA in water, and terbuthylazine-desethyl-2-hydroxy in sediment (Table 2). Moreover, some TPs of prohibited PPPs were also found in our analyses, such as atrazine-2-hydroxy or imidacloprid-desnitro, despite bans on the use of atrazine throughout the European Union since 2003 (Sass and Colangelo, 2006) and of imidacloprid in France since 2018 (Legifrance, 2018). TPs are thus more persistent than associated parent compounds. Such persistence in the environment poses a real issue, as well as if TPs are more toxic or mobile, and these particular cases should be identified (Escher and Fenner, 2011). The Water Framework Directive (WFD, 2000/60/EC) provides a list of priority substances for which actions should be taken for their removal, and recommends to reduce pollution for other compounds (The European Parliament and the Council of the European Union, 2014). However, the WFD priority list contains only 19 pesticides among 45 substances or groups, and no TPs are referenced. France has sought to improve the WFD list, by including micropollutants that should be monitored. For instance, a nationwide campaign was conducted in 2012 to assess the occurrence of emerging substances (including metolachlor-ESA and metolachlor-OXA) in surface waters (OFB, 2020). Analyses as proposed in this

work as well as in other recent studies (Fonseca et al., 2019; Kiefer et al., 2019; Reemtsma et al., 2013; Rousis et al., 2017) underscore the need to increase the number of monitored compounds and identify relevant TPs to be included. Special attention should be paid to TPs that are present in higher concentrations than parent molecules. Also, in a recent opinion report about the assessment of relevant TPs in water intended for human consumption, the French Agency for Food, Environmental and Occupational Health & Safety recommended assessing the relevance of TPs according to the sanitary risk they pose to consumers (ANSES, 2019). Other authors proposed a method to prioritize TPs based on the use, toxicity, and environmental fate of the parent molecules (Melin et al., 2020). In regard to the environment, the selection of relevant TPs should be based on ecotoxicological risks.

#### **4.2. Fish compartment**

Despite the large number of PPPs and TPs detected in the abiotic compartments (15 out of the 20 PPPs and 18 out of the 20 TPs investigated, [Table 2](#)), only a few were found to accumulate in fish. Our results primarily revealed the presence of benzamide in almost all samples and that of prosulfocarb mostly at TF. Sporadically, tebuconazole, isoproturon-monodesmethyl, and imidacloprid-desnitro were quantified at TF. [These results showed that some molecules, notably prosulfocarb and benzamide, can accumulate in organisms.](#)

[In the fillet of \*C. carpio\*, benzamide, prosulfocarb, and less frequently imidacloprid-desnitro and isoproturon-monodesmethyl were found, highlighting that these contaminants can accumulate in the edible part of the fish. For other species, only the whole body, including the gastrointestinal tract, was investigated. This whole body analysis is well representative of trophic transfer in aquatic environments as](#)



piscivorous fish or birds consume entirely prey fish (e.g. *S. erythrophthalmus* or *T. tinca*). Tebuconazole was only found in the whole bodies of *S. erythrophthalmus* and *T. tinca*, and we could not determine whether this fungicide accumulated in the fish flesh or the digestive contents.

These compounds should be closely monitored as it cannot be excluded that there is an ecotoxicological risk. Particular attention should be paid to prosulfocarb and benzamide, which are found in fillets of *C. carpio*, and which may therefore pose a risk to consumers. In view of these results, we recommend that future research be carried out to assess this risk.

This work carried out on benthic and pelagic fish showed that despite the diversity of molecules detected in the environment, these fish are lightly contaminated. These findings contrast with studies conducted a few years ago showing that **freshwater fish accumulate large number pesticides or other contaminants** (Brodeur et al., 2017; Corcellas et al., 2015; Ernst et al., 2018; Oliveira et al., 2015; Pico et al., 2019; Roche et al., 2009). Such c between the results is most likely due to the evolution of the properties of the pesticides used today. Indeed, Lazartigues et al. (2013a) showed, under laboratory conditions, low accumulation in the muscle tissue of *C. carpio* and *P. fluviatilis* exposed to 13 PPPs (three of which –dimethachlor, metazachlor, and isoproturon– were also analyzed in our study) *via* their diet. These authors attributed the low accumulation rates to the fact that the PPPs used at the time, and still in use today, generally had log Kow values lesser than 5. **In the present work all analytes presented the same feature**, as maximum log Kow was approximatively 4.7 for prosulfocarb and fipronil-sulfone, and as approximately 87% had a log Kow value < 4 (Table A.9, Kim et al., 2021). **Indeed, we aimed principally to inform on polar compounds occurrence, such as TPs, which are uncommonly**

monitored in the environment and particularly in biotic matrices. Thus, our list of analytes was not fully representative of substances potentially present in the fishpond notably regarding hydrophobic ones. It could explain why few contaminants were detected in fish. For example, Corcellas et al. (2015) analyzed 42 individuals composed of various species from four Iberian River basins and detected 9 out of 12 pyrethroids. This higher number of found compounds can be explained by their log Kow comprised between 4.73 (tetramethrin) and 6.8 (bifenthrin) and much more important than those analyzed in our work (Table A.9, Kim et al. 2021). Moreover, the total number of detected contaminants is dependent of the number of fish samples. Herein, 29 and 37 individuals were obtained at T0 and TF, respectively. However, as 3 species were collected, it could impair the probability of detection. For instance, Ernst et al. (2018) detected 30 compounds with log Kow comprised between 0.8 (acetamiprid) and 5.5 (amitraz) by analyzing 70 pesticides in muscle tissue of 143 out of 149 fish.

However, little accumulation of contaminants does not mean that organisms living in the fishpond are not subjected to toxicological effects induced by exposures to PPP and TP mixtures. In Southern Brazil, a field study conducted in a rice-fish system revealed oxidative stress in *C. carpio* induced by pesticide mixtures (lambda-cyhalothrin, thiamethoxam, clorantprilprole, tebuconazole, and trifloxystrobin) (Clasen et al., 2018). Tebuconazole was one of the five compounds consistently quantified in all our water and sediment samples (with atrazine-2-hydroxy, flufenacet-ESA, and metazachlor-ESA and OXA, Table 2). In Argentina, genotoxic and hematological impacts were observed in *P. mesopotamicus* produced in ponds near agricultural lands treated with several PPPs including atrazine, metolachlor and metsulfuron (Brodeur et al., 2021). Considering the diversity of PPPs and TPs

detected in abiotic matrices in our study, it would be worthwhile to carry out additional studies to evaluate the toxicological effects of these contaminants on fish at our sampling sites and more generally in headwater streams, exposed to agricultural contaminants. Our results provide information on contamination combinations and concentrations currently found in the environment which could be used in environmental toxicology studies to have a clear understanding of the potential effects of agricultural contaminants on the environment.

Benzamide concentration was significantly lower at TF compared to T0 in *T. tinca* (Fig. 1). Although not as significant, the same decreasing trend in the concentration of benzamide was observed in the other fish species. Benzamide is produced from degradation pathways of various pesticides such as azinphos-methyl (Engelhardt et al., 1984) or dichlobenil (Holtze et al., 2007), both banned active compounds (European Commission, 2016). The fish farmer does not use any treatment product that could produce this molecule; therefore, we could not trace the source of this contamination but could only note its possible accumulation in fish and its elimination after a production season in the pond. The fish were assumed to have been exposed to benzamide or a parent compound (metabolized and stored in organisms) before their arrival in the fishpond. However, we did not find any evidence of this potential former contamination. Moreover, there is little information on benzamide in the environment. In this work, its non-detection in water may be explained by the fact that it was the only substance presenting the highest LOD of 25 ng.L<sup>-1</sup> (Table 1). In sediment, this TP was quantified in all samples. Various hypotheses could explain the decrease in its concentration observed in fish between T0 and TF: (i) a dilution effect caused by fish growth, but this would mean that the TP sorbed in sediment was not bioavailable (Table 2), (ii) a direct excretion and sorbing to sediment particles, or

(iii) a metabolism could also be presumed, but not confirmed as studies on benzamide detoxification processes are scarce in the scientific literature. The only available works were conducted on rabbits by Bray et al. in the 1940s and 50s, and showed the conversion of benzamide into conjugated benzoic acid (Bray et al., 1951). Future research is warranted to clarify its fate in aquatic environments.

The second compound whose concentration was found to vary greatly in fish was prosulfocarb. In contrast to benzamide, a significant increase in concentrations was observed in all fish whole bodies after fishpond exposure (Fig. 2). Prosulfocarb is a pre-emergence herbicide applied in large quantities to cereal and potato crops and known to reach other parcels by volatilization, vapor drift, or surface runoff (Devault et al., 2019). Its half-life in outdoor stagnant ditch was shorter (2.9 d, 20 °C) than those obtained in hydrolysis and photolysis studies conducted in water-sediment systems under laboratory conditions, suggesting a major role of biodegradation (Adriaanse et al., 2013). Moreover, in natural waterbodies, prosulfocarb is known to quickly sorb to sediment, where it is persistent. In fact, it has a high  $K_{foc}$  value of between 1,367 and 2,339 L.kg<sup>-1</sup>, showing a high sorbing potential to sediment and suspended particles (EFSA, 2007). These observations are in accordance with the low prosulfocarb maximum concentration and FOQ obtained in water compared to those in sediment samples. Organisms may have been exposed *via* ingestion of contaminated sediment or preys, and/or contact. Lastly, even if no significant difference was highlighted (certainly caused by the use of non-parametric tests) prosulfocarb concentrations tended to be lower in the fillet than in the whole body of *C. carpio* at TF (Fig. 2). As Mackay et al. (2018) showed, such variation might have been due to the lipid content, which was significantly lower in muscle at TF (Table

A.8). It also coincides with the greater BCF value of prosulfocarb in fish whole body ( $700 \text{ L.kg}^{-1}$ ) compared to fish fillet ( $480 \text{ L.kg}^{-1}$ ) (EFSA, 2007; Lewis et al., 2016).

The European Union Pesticide Regulation No. 396/2005 sets maximum residue levels (MRLs) of pesticides for food agricultural products based on their toxicity, their expected maximum concentrations, and the different diets of Europeans (The European Parliament and the Council of the European Union, 2005). Nevertheless, there are no established MRLs for fish products, because they are based on Good Agricultural Practices. Thus, pesticides quantified in fish cannot be related to these thresholds but to extraneous MRLs (EMRLs) (Pérez-Parada et al., 2018). However, no EMRL are referenced in the Codex Alimentarius for freshwater fish (FAO and WHO, 2020). As other studies have done (Brodeur et al., 2021; Pérez-Parada et al., 2018), we bring evidence of PPP and TP presence in edible fish. It would be advisable to conduct further field investigations to obtain more information about contaminants occurring in the environment which are likely to accumulate in such organisms, so as to control their safety especially when exposed to conventional crops nearby (Brodeur et al., 2021). This will help incorporate specific and necessary EMRLs for fish. Even though few substances were detected in fish during this work, the findings are a warning signal to government authorities to take action to either regulate these compounds or limit their transfers by providing specific environmental or production management guidelines. If we wish to ensure consumer safety of aquatic products and the protection of aquatic fauna, priority attention should be given to these substances.

## 5. Conclusions

Our work aimed to provide new data on agricultural contaminant mixtures occurring in water, sediment, and fish in a small lentic waterbody. In abiotic compartments, the results revealed the importance of including TPs in environmental monitoring due to their high quantified concentrations and rates, regardless of concentrations of their parent compounds or their authorization of use status. Contaminants, and especially TPs, that showed the highest measured concentrations in the present study should be examined in future (eco)toxicological studies to obtain precise results **in order to** better assess risk. It would help identify the relevant TPs that need priority monitoring in the environment. In fish, few compounds were detected. However, these very organisms accumulated prosulfocarb significantly after exposure to the fishpond, probably through contaminated sediment particles and/or preys. Setting specific concentration thresholds for fish products is therefore key, as is providing information on priority compounds to be monitored or regulated.

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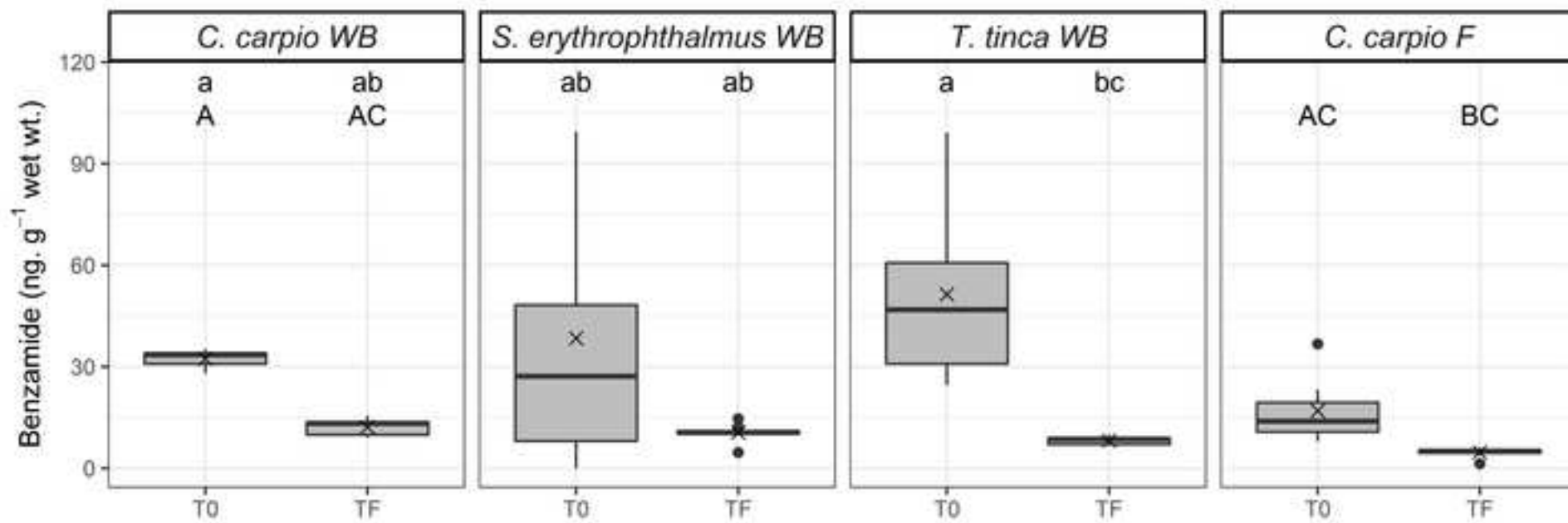


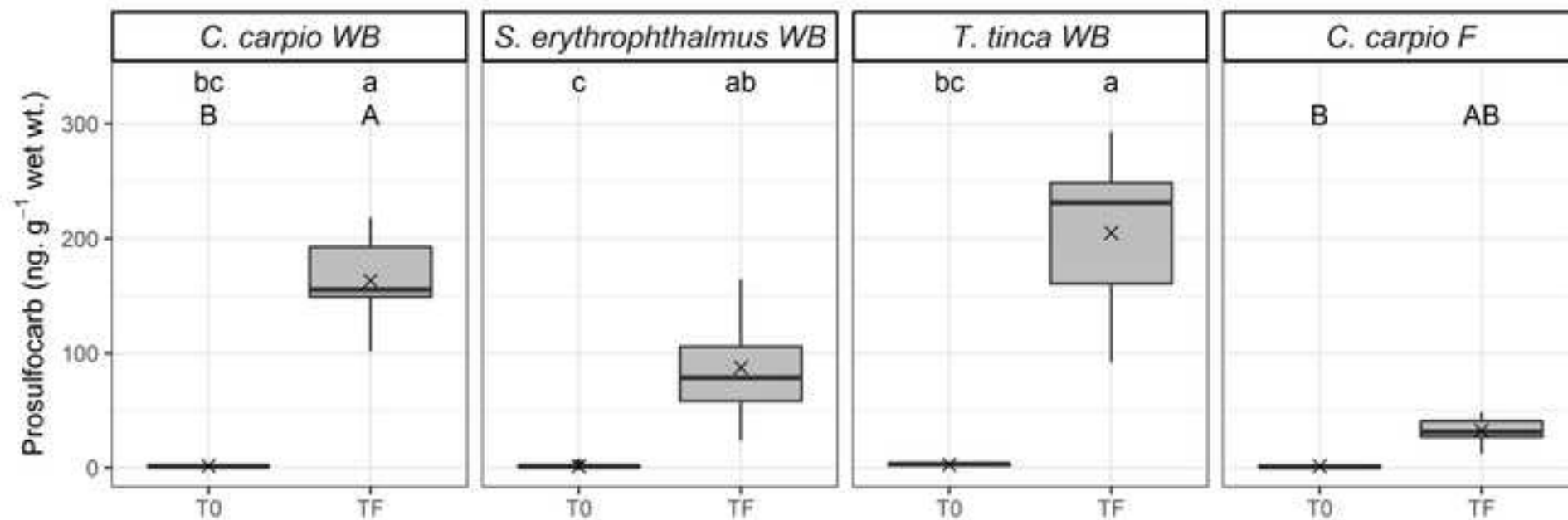
**Table 1.** List and limits of detection/limits of quantification of analyzed compounds in water ( $\text{ng.L}^{-1}$ ), sediment ( $\text{ng.g}^{-1}$  dry wt.), and fish ( $\text{ng.g}^{-1}$  dry wt.) matrices.

**Table 2.** Concentrations of detected compounds in water ( $\text{ng.L}^{-1}$ ) and sediment ( $\text{ng.g}^{-1}$  dry wt.).

**Fig. 1.** Benzamide concentrations ( $\text{ng.g}^{-1}$  wet wt.) in fish whole body (WB) and fillet (F). Results are expressed as boxplots. Concentrations below LOD were estimated as null, and those comprised between LOD and LOQ were set to LOQ/2. Marks symbolize means. Lowercase letters are used to indicate significant differences between benzamide concentrations found in fish WB, while capital letters are used for *C. carpio* WB and F comparisons ( $p\text{-value} < 0.05$ ).

**Fig. 2.** Prosulfocarb concentrations ( $\text{ng.g}^{-1}$  wet wt.) in fish whole body (WB) and fillet (F). Results are expressed as boxplots. Concentrations below LOD were estimated as null, and those comprised between LOD and LOQ were set to LOQ/2. Marks symbolize means. Lowercase letters are used to indicate significant differences between prosulfocarb concentrations found in fish WB, while capital letters are used for *C. carpio* WB and F comparisons ( $p\text{-value} < 0.05$ ).





**Table 1.** List and limits of detection/limits of quantification of analyzed compounds in water (ng.L<sup>-1</sup>), sediment (ng.g<sup>-1</sup> dry wt.), and fish (ng.g<sup>-1</sup> dry wt.) matrices.

Compound	LODs/LOQs		
	Water	Sediment	Fish
Acetochlor (H)	10/20	0.06/0.12	9.9/29.7
Acetochlor-OXA	5/10	0.03/0.06	6.3/19
Alachlor (H)	10/20	NA <sup>a</sup>	4.5/13.6
Acetochlor-alachlor-ESA	5/10	0.03/0.06	10.4/31.1
Atrazine (H)	2.5/5	0.015/0.03	1/3.1
Atrazine-2-hydroxy	5/10	0.03/0.06	0.4/1.3
Boscalid (F)	2.5/5	0.015/0.03	13.2/39.7
Bentazone (H)	2.5/5	0.015/0.03	0.3/0.8
Chlorotoluron (H)	2.5/5	0.015/0.03	0.6/1.7
Dimethachlor (H)	2.5/5	0.015/0.03	0.6/1.8
Dimethachlor-ESA	2.5/5	0.015/0.03	19.6/58.7
Dimethenamid (H)	5/10	0.03/0.06	0.4/1.1
Dimethenamid-ESA	2.5/5	0.015/0.03	11.8/35.4
Fenthion (I)	10/20	0.06/0.12	21.3/64
Fipronil (I)	2.5/5	0.015/0.03	NA/2.6
Fipronil-sulfone	2.5/5	0.015/0.03	NA/1.1
Flufenacet (H)	2.5/5	0.015/0.03	1.3/3.9
Flufenacet-ESA	2.5/5	0.015/0.03	7.7/23
Flufenacet-OXA	5/10	NA <sup>a</sup>	15.6/46.8
Imidacloprid (I)	5/10	0.03/0.06	12.1/36.3
Imidacloprid-desnitro	2.5/5	0.015/0.03	0.7/2.1
Isoproturon (H)	2.5/5	0.015/0.03	NA/4.5
Isoproturon-monodesmethyl	2.5/5	0.015/0.03	0.5/1.5
MCPA (H)	5/10	0.03/0.06	4.9/14.6
Metazachlor (H)	2.5/5	0.015/0.03	0.4/1.1
Metazachlor-ESA	10/20	0.06/0.12	11.6/34.8
Metazachlor-OXA	10/20	0.06/0.12	74.2/222.5
Metsulfuron-methyl (H)	2.5/5	0.015/0.03	4.8/14.5
Prosulfocarb (H)	2.5/5	0.015/0.03	NA/13.9
Metolachlor (H)	2.5/5	0.015/0.03	NA/16
CGA-50267	2.5/5	0.015/0.03	0.8/2.3
Metolachlor-ESA	2.5/5	0.015/0.03	17.1/51.3
Metolachlor-OXA	10/20	0.06/0.12	8.9/26.8
Tebuconazole (F)	2.5/5	0.015/0.03	0.9/2.7
Terbuthylazine (H)	2.5/5	0.015/0.03	0.6/1.8
Terbuthylazine-desethyl	2.5/5	0.015/0.03	0.7/2.2
Terbuthylazine-desethyl-2-hydroxy	2.5/5	0.015/0.03	2.2/6.5
3,5,6-trichloro-2-pyridinol	10/20	0.06/0.12	137.4/412.1
Benzamide	25/50	0.15/0.3	30.6/10.8
Chloridazon-methyl-desphenyl	5/10	0.03/0.06	5.3/15.9

F: Fungicide, H: Herbicide, I: Insecticide, LODs/LOQs: Limits of detection/Limits of quantification, NA: Not available, <sup>a</sup> No concentration assessment as recoveries were null. In grey: TP.

**Table 2.** Concentrations of detected compounds in water (ng.L<sup>-1</sup>) and sediment (ng.g<sup>-1</sup> dry wt.).

Compound	Water			Sediment		
	FOD/FOQ	Conc. range	Mean ± SEM <sup>a</sup>	FOD/FOQ	Conc. range	Mean ± SEM <sup>a</sup>
Atrazine-2-hydroxy	100/100	[20.4, 81.1]	42.1 ± 6.2	100/100	[0.15, 0.4]	0.22 ± 0.02
Boscalid	100/63	[<LOQ, 12.2]	-	100/100	[0.08, 0.71]	0.28 ± 0.04
Bentazone	33.3/0	[<LOD, <LOQ]	-	25.9/3.7	[<LOD, 0.04]	-
Chlorotoluron	81.5/48.1	[<LOD, 11.1]	-	100/100	[0.35, 1.12]	0.62 ± 0.03
Dimethachlor	11.1/7.4	[<LOD, 7.95]	-	25.9/0	[<LOD, <LOQ]	-
Dimethachlor-ESA	100/100	[9.6, 43.7]	26.9 ± 3.4	16.7/3.7	[<LOD, 0.14]	-
Dimethenamid	31.5/22.2	[<LOD, 1710]	-	33.3/25.9	[<LOD, 2.64]	-
Dimethenamid-ESA	96.3/96.3	[<LOD, 28.4]	15.7 ± 2.3 <sup>c</sup>	0/0	[<LOD, <LOD]	-
Fipronil-sulfone	0/0	[<LOD, <LOD]	-	3.7/0	[<LOD, <LOQ]	-
Flufenacet	44.4/37	[<LOD, 153]	-	100/88.9	[<LOQ, 2.2]	-
Flufenacet-ESA	100/100	[190, 900]	502 ± 42.6	100/100	[0.15, 0.71]	0.43 ± 0.02
Flufenacet-OXA	100/100	[58.9, 352]	144 ± 15.7	NA	NA	NA
Imidacloprid	0/0	[<LOD, <LOD]	-	35.2/0	[<LOD, <LOQ]	-
Imidacloprid-desnitro <sup>b</sup>	0/0	[<LOD, <LOD]	-	100/100	[0.05, 0.19]	0.09 ± 0.01
Isoproturon	3.7/0	[<LOD, <LOQ]	-	100/100	[0.17, 0.84]	0.36 ± 0.02
Isoproturon-monodesmethyl <sup>b</sup>	0/0	[<LOD, <LOD]	-	100/100	[0.06, 0.33]	0.13 ± 0.01
MCPA	11.1/11.1	[<LOD, 80]	-	11.1/0	[<LOD, <LOQ]	-
Metazachlor	38.9/38.9	[<LOD, 39.2]	-	96.3/92.6	[<LOD, 0.15]	0.07 ± 0.01 <sup>c</sup>
Metazachlor-ESA	100/100	[88.9, 548]	256 ± 40.8	100/100	[0.14, 0.72]	0.32 ± 0.04
Metazachlor-OXA	100/100	[202, 1063]	519 ± 57	100/100	[0.25, 1.56]	0.87 ± 0.07
Metolachlor	33.3/33.3	[<LOD, 34.2]	-	100/74.1	[<LOQ, 0.21]	-
CGA-50267	0/0	[<LOD, <LOD]	-	7.4/0	[<LOD, <LOQ]	-
Metolachlor-ESA	100/100	[22.4, 73.8]	47.1 ± 3.7	79.6/79.6	[0.07, 0.26]	-
Metolachlor-OXA	100/100	[30.9, 98.4]	60.8 ± 3.63	22.2/0	[<LOD, <LOQ]	-
Metsulfuron-methyl	11.1/11.1	[<LOD, 7.1]	-	0/0	[<LOD, <LOD]	-
Prosulfocarb <sup>b</sup>	48.1/33.3	[<LOD, 14.2]	-	100/100	[0.58, 3.3]	1.48 ± 0.19
Tebuconazole <sup>b</sup>	100/100	[11.1, 59.8]	31.7 ± 3.59	100/100	[0.97, 2.92]	1.75 ± 0.14
Terbuthylazine	7.4/0	[<LOD, <LOQ]	-	0/0	[<LOD, <LOD]	-
Terbuthylazine-desethyl	11.1/0	[<LOD, <LOQ]	-	0/0	[<LOD, <LOD]	-
Terbuthylazine-desethyl-2-hydroxy	0/0	[<LOD, <LOD]	-	87/59.3	[<LOD, 0.1]	-
3,5,6-trichloro-2-pyridinol	0/0	[<LOD, <LOD]	-	81.5/48.1	[<LOD, 0.43]	-
Benzamide <sup>b</sup>	0/0	[<LOD, <LOD]	-	100/100	[3.03, 5.44]	4.2 ± 0.2
Chloridazon-methyl-desphenyl	0/0	[<LOD, <LOD]	-	13/7.4	[<LOD, 0.08]	-

FOD/FOQ: Frequency of detection/Frequency of quantification (%), LOD/LOQ: Limit of detection/Limit of quantification, <sup>a</sup> Determined when FOQ > 90%, <sup>b</sup> Detected in fish samples, <sup>c</sup> Estimated using substitution (<LOD = 0, <LOQ = LOQ/2), NA: Not available. Compounds not detected in both matrices are not presented. In grey: TP.