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Pesticide Distribution in Pond Sediments from an Agricultural Catchment (Auradé, SW France) †

Betty Chaumet [1,2,3,*], Jean-Luc Probst [1,2,3], Pierre Eon [1], Virginie Payré-Suc [1,2,3], Franck Granouillac [1,2,3], Thierry Camboulive [1,2,3], David Riboul [1], Corinne Pautot [1], Marie-Josée Tavella [1], Benjamin Trochon [1] and Anne Probst [1,2,3,*]

[1] Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, 31000 Toulouse, France
[2] LTSER Zone Atelier Pyrénées-Garonne, CNRS, University of Toulouse, 31000 Toulouse, France
[3] LTER Bassin Versant Auradé, IR OZCAR, CNRS, University of Toulouse, 31000 Toulouse, France
* Correspondence: betty.chaumet@toulouse-inp.fr (B.C.); anne.probst@ensat.fr (A.P.)

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Abstract: Currently, pesticides are massively used in agricultural areas end up in watercourses, as they are usually final receptacles of organic contamination. A large number of wetlands such as ponds occurred in agricultural catchments. They are dynamic and complex systems which contains different compartments like the water column, sediments and biota. The sediment compartment can store contaminants according to their physicochemical properties, but this process is continuously challenged because of settling and resuspension mechanisms. The role of the sediments regarding pesticides behavior and their fate is still poorly investigated. Our study aimed to fill this gap, particularly considering the Bassioué pond, which is located in the carbonated agricultural upper sub-catchment of the Auradé critical zone observatory (Gers, France), with a wheat/sunflower crop rotation and a steep slope enhancing erosion phenomenon. We focused on pesticide storage in the sediments which represent the main compartment due to the environmental conditions. Our current objective was to understand (i) how and where pesticides are stored in the sediments, and (ii) the relationship with the characteristics of sediments, supposed to be highly involved in the storage and degradation of pesticides. Two field campaigns were carried out to collect sediment samples within a regular quadrat from the inlet to the outlet of the pond in autumn 2019 and summer 2020 at different depth. A set of three pesticide was quantified as well as sediment texture. The results highlighted that sediment particle size distribution varied between upstream and downstream of the pond: from the finest to the coarsest; as did the spatial distribution of pesticides. This reveled that pesticides were partly controlled by their physicochemical properties: most hydrophilic pesticides had greater affinity with the finest fractions of the sediments. A difference in pesticide storage according to the depth has been observed, especially for boscalid ($\log K_{OW} = 3$) which was found in greater quantities in the deepest samples, with increasing coarse silt content. Finally, a seasonal effect was also observed on pesticide levels, as their presence was highly driven by firstly their uses in the catchment and secondly by the soil erosion occurring during intense spring flood events. This work provides new knowledge on the role of ponds in pesticide storage, dissipation and transfer downstream, which can·be used for agricultural landscape management.

Keywords: wetland; pesticides; bottom sediments; agricultural catchment; storage; spatial distribution

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1. Introduction

Owing to their ubiquitous presence in soils and watercourses, pesticides represent a major issue in environmental risk assessment, particularly in agricultural areas. Indeed, for many years now, pesticides have been massively detected in agricultural catchment areas, notably in wetlands [1,2]. Wetlands play an essential role in the transfer of contaminants and in the quality of aquatic systems [3]. Among these wetlands, ponds, natural or artificial are known to participate in pesticide dissipation as they are composed of many compartments which can interact with these contaminants. For example, the water column can transport pesticides, sediment and vegetation can store and possibly degrade these contaminants [4]. Thus, they represent a dynamic and complex environment, which could be used for a better land management for pesticide reduction in agricultural zones [5].

Among the processes inherent in this system, storage mechanisms play a major role in the dissipation of pesticides, particularly in bottom sediments. In erosive areas, this compartment is constantly in undergoing evolution due to sedimentation and resuspension processes. Thus, the upper layer of sediment which is in constant interaction with the water column is the most reactive.

Depending of their configuration, ponds can extend the retention time of water and by extension, of contaminants [6,7]. Pesticides can be sorbed onto suspended particles and settle over the time between the upstream and downstream part of the pond. This process can be strongly affected by the particles size distribution (clays, silts, sands, gravels) [8,9]. Indeed, the larger the particles are (gravel or sand type), the higher their upstream sedimentation when they get into the pond [10]. Conversely, smaller particles (such as clays or silts) generally settle further downstream of the pond. Other parameters may influence pesticide storage in sediments, such as the carbon content [11] or the physicochemical properties of these molecules [12]. Pesticides with high $\log K_{OW}$ (<3) present a greater affinity with sediment's particles and then are more likely to be adsorbed [13,14]. It was also evidenced that fine particles such as silts or clays have a greater adsorption capacity due to their larger specific surface areas [15].

Despite these previous mechanistic studies about pesticides and their interactions with sediments, very few studies focused on their fate in a natural very complex system that are wetlands. A lot remains to be studied in order to better understand where and why pesticides will be stored in the sediment compartment. This is why our study aims to characterize the role of ponds in pesticides dissipation by storage in the sediments in agricultural lands. We investigated the spatial distribution of pesticides in the upper layers of the sediments of a small upstream pond and the relationship with their physicochemical characteristics, to understand their behavior.

2. Material and Methods

2.1. Study Site and Field Campaigns

The studied pond is located in the upstream part of the carbonated Auradé catchment (Gers, SW France) which is a French eLTER site. It is mainly cultivated with a yearly rotation of sunflower and wheat, and undergoes a significant soil erosion because of steep slopes and significant storm events in spring [16,17] (Figure 1). This pond is 60 m long, 11 to 21 m wide with 0.5 m of water column and 3 m of sediment layer depth. Following several erosive storm events, the sediment accumulated in the pond has led to a reduction of the water level of 30 to 50 cm depth depending on the season. A major flood event in 2018 has contributed to the formation of a sediment bed at the entrance of the pond, creating a small secondary upstream pond (named PM) of 7.5 m long and 5 m wide connected to the major one. On this sedimentary bed, a natural vegetation has taken place.

Two core sampling campaigns were carried out in autumn 2019 (November 18th) and the following summer (July 3rd, 2020). Each time, eight cores of the upper sediment layer were collected using a UWITEC core drill (Ø: 8.8 cm) according to a previously established regular quadrat (Figure 1). During both sampling campaigns, surface sediments were collected (the first 2 cm). Deeper sediments from the cores were also collected in the second campaign: from 2 to 12 cm depth (called "Middle") and from 12 to 17 cm depth (called "Bottom").

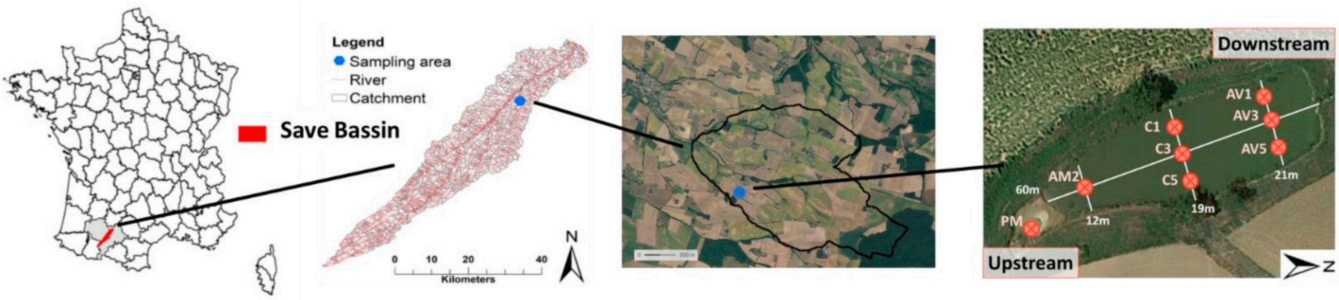

Figure 1. Location of the field study site at (from left to right): country scale, basin scale from Wu PhD, sub-catchment scale (map from Google map) and pond scale (map from Google map) with sampling points.

2.2. Sample Preparation and Analysis

Once in the laboratory, the samples were dried at room temperature and disintegrated smoothly using an agate mortar and pestle, quartered and an aliquot was collected for micro-granulometry analysis on the bulk sample. The rest of the samples was sieved in order to collect only the fine fraction (<63 µm) pesticide analysis. Micro-granulometry was determined by laser diffraction (LA920-V2, Horiba) according to ISO 13,320 guideline to determine the percentage of the sediment fractions: i.e., clays (0–2 µm), fine (2–20 µm) and coarse (20–63 µm) silts, sands (63 µm–2 mm) and gravels (<2 mm).

Three pesticides were targeted and they have been chosen because of their different physicochemical properties ranging from hydrophilic and highly soluble (metolachlor: $\log K_{OW} = 2.9$, solubility = 530 $mg \cdot L^{-1}$), to hydrophilic and poorly soluble (boscalid: $\log K_{OW} = 3$, solubility = 4.6 $mg \cdot L^{-1}$), to moderately hydrophobic and poorly soluble (tebuconazole: $\log K_{OW} = 3.7$, solubility = 36 $mg \cdot L^{-1}$). Also, they are still intensively used in the catchment on different culture type and they were analyzed in surface and deep core sediment samples. They were extracted and quantified from sediment matrix using methanol and adding a stock solution containing the associated deuterated internal standards. Then the samples were agitated (5 min vortex at 1200 rpm, 30 min of ultrasound, and 5 min vortex at 1200 rpm) and centrifugated (6000 rpm, 20 min at 4 °C) in order to collect the supernatant for the second step of extraction. Contaminants were extracted from methanol matrix to SBSE bar (Stir Bar Sorptive Extraction) following a 3-h agitation. Finally, pesticides were thermo-desorbed and quantified using a GC-TD-MS/MS (TRACE 1300—TSQ8000EVO, Thermo Fischer, Waltham, MA, USA). Due to the large number of samples, only one replicate was analyzed by sampling point, depth and season.

3. Results

3.1. Sediment Characteristics

For all the sediment samples (collected at the "Surface" and "Bottom" of the core), the micro-granulometry indicated that for most of the samples, the fine silts (2–20 µm) were predominant. With the exception of the "PM" site for the "Bottom" sediment samples for the summer 2020 campaign, the percentage of fine silts varied from 58 to 82% (Table 1). Results were similar for the autumn campaign. This percentage increased from upstream to downstream for the surface and bottom samples. On the other hand, a high percentage of coarser fraction was observable at the most upstream point of the pond ("PM") for the deeper samples of the second campaign. All of these results are consistent with the principle that larger and heavier particles settle more rapidly than smaller ones, and therefore in the upstream pond [18].

Table 1. Distribution of the different size fractions in the sediments in percentage at the surface and at the bottom of the different cores for the July 2020 campaign.

		Clay (%)	Fine Silt (%)	Coarse Silt (%)	Sand (%)	Gravel (%)
Surface	AV1	12.1	73.8	6.2	4.7	3.2
	AV3	13.7	80.8	3.8	1.1	0.6
	AV5	14.7	80.9	4.2	0.2	0.0
	C1	11.8	78.5	7.8	1.7	0.3
	C3	11.0	81.0	6.0	1.7	0.3
	C5	11.3	82.4	4.1	1.7	0.5
	AM2	7.6	65.6	17.5	6.8	2.5
	PM	9.7	65.1	17.5	7.2	0.5
Bottom	AV1	19.1	71.3	7.7	1.8	0.1
	AV3	20.4	67.3	7.2	3.8	1.3
	AV5	20.9	69.5	6.8	2.7	0.1
	C1	19.0	64.4	9.2	6.7	0.7
	C3	19.9	65.6	9.9	3.1	1.5
	C5	17.9	71.1	7.2	3.4	0.5
	AM2	17.4	58.3	10.6	12.5	1.2
	PM	3.2	15.9	3.2	4.8	72.8

3.2. Pesticide Storage in Sediments

Metolachlor concentrations averaged 2.6 ± 0.3 $\mu g~kg^{-1}$, for the samples collected at the surface during the first campaign, and 1.3 ± 0.1 and 3.6 ± 0.5 $\mu g~kg^{-1}$ at the surface and depth of the second campaign, respectively. The concentrations were respectively 5.5 ± 0.4, 3.3 ± 0.1 and 10.8 ± 1.3 $\mu g~kg^{-1}$ for boscalid and 8.1 ± 0.6, 21.7 ± 2.6 and 8.3 ± 1 $\mu g~kg^{-1}$ for tebuconazole, in the same order. These data illustrated that pesticides were not accumulated in the same way according to the season (due to different application periods) and between surface and depth, with molecule specificity. However, these values remain relatively low compared to what can be found in Mediterranean areas with high agricultural activity, with pesticide concentrations of several hundred g per kg [19].

4. Discussion

4.1. Role of Sediment Texture

The nature of the sediments plays an important role in pesticide storage distribution. Firstly, a positive linear relationship was observed between the of boscalid and metolachlor concentrations and the percentage of clay (relative to the fine fraction <63 µm, Figure 2C) of the sediment, with an even higher slope for boscalid. Due to its high sorption capacity [8,20], clay is one of the main controlling factors for boscalid and metolachlor storage in the sediments. However, this was not observed for tebuconazole with clays (not shown), nor with the fine silt fraction, which is the dominant fraction (Figure 2A). Several studies have demonstrated that numerous environmental factors can impact contaminant sorption in the sediment such as the pH and carbonate content [21–23]. Since our studied site is surrounded by highly carbonated soil [16], this might have modified the sorption conditions and processes of tebuconazole in sediments. Surprisingly, boscalid was also positively related to the coarse fraction of silt (Figure 2B), if we except the sites from the small upstream pond, which were very enriched in coarse fractions. This suggests a high persistence of this molecule in sediment which is supported by the long as half-life time found in soils about 246 days [24].

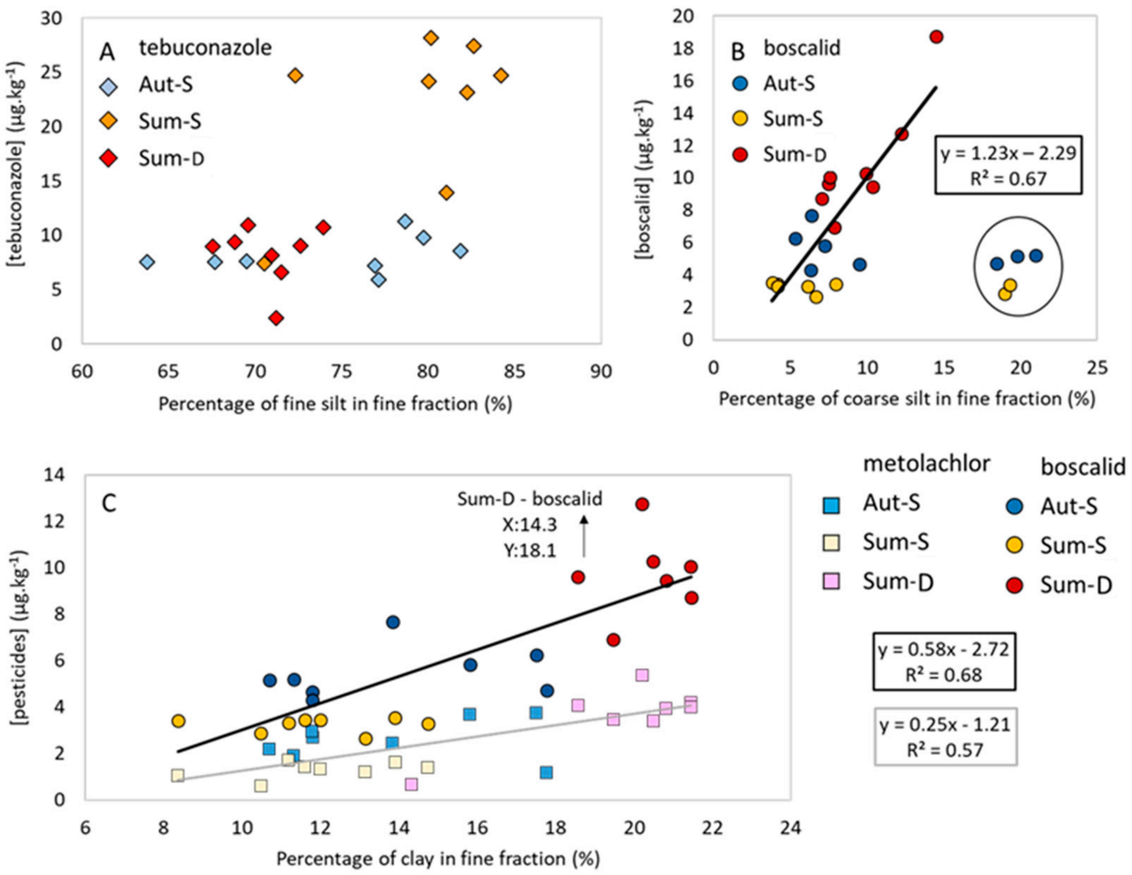

Figure 2. Relationships between pesticide concentrations in sediments (in µg·kg^{-1}) and the percentage of the different granulometric fine fractions for the different sampling seasons (Sum: summer; Aut: autumn) and depths (S: surface sediment; D: deep sediment). (**A**) tebuconazole *versus* fine silts, (**B**) boscalid *versus* coarse silts, (**C**) boscalid (circles) and metolachlor (squares) *versus* clays. All percentages are relative to the total fine fraction (<63 µm). The linear regressions of the set of points are represented by black lines for boscalid (**B**), excepted encircled outliers and (**C**), except one sample out of Y-axis) and grey line for metolachlor (**C**).

4.2. Seasonality Effect

A seasonal effect was noticeable, as observed for tebuconazole with concentrations two times higher in surface samples collected in summer compared with autumn (Figure 2A). These higher concentrations could be explained by transport during spring flood event [25] since it was used generally in early spring as a fungicide on cereal crops (predominant in the upstream catchment). The lower concentrations in autumn might be due to degradation phenomenon including biodegradation by plants [26] and/or dilution processes with increasing stream flow. However, at this stage, the results cannot explain what is the controlling factor for tebuconazole. The redox potential or the pH could influence the storage of this pesticide in the sediments [13,27].

The opposite was observed for boscalid and metolachlor (Figure 2C). One of the possible hypotheses to explain this observation would be the link to distinct degradation phenomena (greater activity on the surface) like mineralization by phytoplankton activity [28] or to a migration of these molecules deeper down. These two molecules have a logK_{OW} slightly lower than that of tebuconazole, which could explain their different behavior. For boscalid, one of the possible explanations would also be its relatively rare use in summer.

4.3. Depth Storage Process and Other Influencing Parameters

It was observed that pesticides were not accumulated in the same way according to depth. This was particularly visible for boscalid. For the same sampling location, concentrations were on average three times higher in the bottom of the core than at the surface (for the second campaign). The clay and coarse silt enrichment can be explained these higher boscalid concentrations with depth (see Section 4.1). The same pattern was observed for clay enrichment and metolachlor content. As described by Farenhorst et al. [29], some pesticides do not have the same sorption capacity depending on the depth considered. Indeed, the processes in depth can differ and be affect by the physicochemical conditions of the surrounding environment such as the sediment particle size distribution, the redox potential, pH, carbonate and oxide content [22].

Organic carbon did not have a marked influence on pesticide storage in those sediments since no correlation between particulate organic carbon content and pesticide concentrations could be demonstrated. Indeed, the organic carbon content did not exceed 1% [30], which is really similar to the soil content [31]. Although studies have demonstrated the influence of organic carbon on pesticide sorption [11,32], in this case, this parameter was not considered as a controlling factor.

5. Conclusions

This study has characterized the spatial storage of pesticides in relation with the distribution of sediment texture, in a pond in an agricultural area. Both on the surface and at the bottom, fine silt was the main fraction almost all over the pond, but an increase of the coarser fraction was visible by the outlet of the pond. Beside its majority presence, the fine silt fraction was not responsible for pesticide accumulation in the sediments. Results highlighted that clays controlled metolachlor and boscalid contents, and with the boscalid being also surprisingly controlled by the coarse fraction. The influence of the seasonality in relation with the period of pesticide application was also highlighted, as the higher concentrations were found in summer after the combo pesticides spreading and intense flood events. Finally, the pesticide enrichment with depth raised new questions about the processes occurring under the surface. New knowledges and hypotheses have been put forward like biodegradation and migration which opens up new scientific perspectives.

This study proved that pesticides can be stored in the sediment compartment which contributes to their dissipation downstream of the pond. However, it was shown that these processes can vary with time and depth thus highlighting the importance of understanding all these mechanisms in order to provide appropriate solutions for agricultural land management.

Author Contributions: B.C. and A.P. conceived and designed the experiments; B.C., A.P., V.P.-S., F.G., T.C., J.-L.P., M.-J.T. and B.T. performed the experiments; P.E., T.C. and B.C. prepared the samples; D.R. and C.P. performed the analysis; B.C., A.P., J.-L.P. and P.E. analyzed the data; B.C. and P.E. wrote the paper; J.-L.P. reviewed and approved the paper; A.P. and J.-L.P. supervised the paper; P.E. and J.-L.P. managed the project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ANR	National Research Agency
eLTER	European Long-Term Ecosystem Research infrastructures
Pestipond	"Role of ponds in the transfer and impact of pesticides in surface waters of the critical zone in agricultural environment". Project funded by the ANR which aims to characterize the role of ponds in pesticide dissipation
rpm	rotation per minute
SW	South-West

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