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HAL Id: hal-03287984

<https://hal.science/hal-03287984>

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Chaumet, Betty[✉] and Probst, Jean-Luc[✉] and Eon, Pierre[✉] and Camboulive, Thierry[✉] and Riboul, David[✉] and Payre, Virginie[✉] and Granouillac, Franck[✉] and Probst, Anne[✉] *Role of Pond Sediments for Trapping Pesticides in an Agricultural Catchment (Auradé, SW France): Distribution and Controlling Factors*. (2021) Water, 13. 1734. ISSN 2073-4441

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Article

Role of Pond Sediments for Trapping Pesticides in an Agricultural Catchment (Auradé, SW France): Distribution and Controlling Factors

Betty Chaumet ^{1,2,3,*} , Jean-Luc Probst ^{1,2,3} , Pierre Eon ¹, Thierry Camboulive ^{1,2,3}, David Riboul ¹, Virginie Payré-Suc ^{1,2,3}, Franck Granouillac ^{1,2,3} and Anne Probst ^{1,2,3,*}

- ¹ Laboratory of Functional Ecology and Environment, University of Toulouse, CNRS, Auzeville Tolosane, 31326 Castanet Tolosan, France; jean-luc.probst@toulouse-inp.fr (J.-L.P.); eonpierre@hotmail.fr (P.E.); thierry.camboulive@univ-tlse3.fr (T.C.); david.riboul@inp-toulouse.fr (D.R.); virginie.payre@toulouse-inp.fr (V.P.-S.); franck.granouillac@univ-tlse3.fr (F.G.)
- ² LTSEZ Zone Atelier Pyrénées-Garonne, CNRS, University of Toulouse, 31326 Castanet Tolosan, France
- ³ LTER Bassin versant Auradé, IR OZCAR, CNRS, University of Toulouse, 31326 Castanet Tolosan, France
- * Correspondence: betty.chaumet@toulouse-inp.fr (B.C.); anne.probst@toulouse-inp.fr (A.P.)

Abstract: In agricultural areas, ponds are suitable wetland environments to dissipate and reduce the occurrence of pesticides in aquatic environments. However, their impact at a catchment scale is still poorly understood. This study aims to determine how these organic contaminants were trapped in a pond located in an agricultural critical zone from SW France (Auradé catchment). The spatial distribution of pesticide concentrations and their different controlling factors were investigated in waters and sediments collected during two distinct seasons. The results highlighted (i) the link between the presence of the molecules and the agricultural practices upstream, (ii) the influence of hydrological/seasonal conditions, especially on hydrophobic molecule accumulation such as tebuconazole, (iii) the key role of clay content in sediments on the control of moderately hydrophilic pesticides (metolachlor and boscalid), but also the unexpected role of coarse particles for boscalid; and (iv) the influence of sediment depth on pesticide storage. Nevertheless, other physico-chemical parameters, such as mineralogical composition of sediment, needed to be considered to explain the pesticide patterns. This study brings a new hypothesis to be investigated in the future about pesticide behaviour in such pond environments.

Keywords: metolachlor; tebuconazole; boscalid; bottom sediments; spatial distribution; seasonality effect; sorption; particle size; partition coefficients



Citation: Chaumet, B.; Probst, J.-L.; Eon, P.; Camboulive, T.; Riboul, D.; Payré-Suc, V.; Granouillac, F.; Probst, A. Role of Pond Sediments for Trapping Pesticides in an Agricultural Catchment (Auradé, SW France): Distribution and Controlling Factors. *Water* **2021**, *13*, 1734. <https://doi.org/10.3390/w13131734>

Academic Editor: George Arhonditsis

Received: 27 May 2021

Accepted: 18 June 2021

Published: 23 June 2021

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1. Introduction

Pesticides are commonly extensively used in traditional agriculture to protect crops from diseases and adventive plants [1,2]. Intensive agriculture may contribute to soil erosion and to pesticide transfer to aquatic environments [3–6]. Some agricultural areas thus undergo a risk for river contamination depending on their typology or uses [7–10]. Indeed, pesticides are transferred from soils to watercourses by many different pathways. They can be transported as dissolved and particulate phases by surface runoff, soil leaching and deep-water drainage [11–13]. The transport in different water phases depends on the physico-chemical properties of pesticides: the ones with a high $\log K_{OW}$ (>3) are more easily sorbed onto suspended particles and sediments [14–16] while those with a lower $\log K_{OW}$ are rather transported in dissolved phases, bound to dissolved organic matter [17–22]. In addition, Gao et al. [23] have shown that the more hydrophobic a molecule is, the more quickly and permanently it is absorbed onto the sediment. It was also demonstrated that the potential sorption of pesticides onto particles depends on the sorption coefficient (K_{OC}) [24].

The surface waters draining a catchment are the final receptacle of any contamination from upstream and the drivers of pollutants downstream. In catchments, some natural wetlands or man-made water reservoir, may take place in disconnection or in connection to the stream waters. A pond is a natural or artificial aquatic system, generally smaller (<2 ha) and shallower (where light penetrates to the bottom) than a lake [25]. These water reservoirs represent a complex dynamic environment [26] which is not fully understood [27]. Particularly, the influence of ponds on the transfer of pollutants downstream remains poorly documented, especially for pesticide dissipation at the catchment scale.

By increasing the residence time of pesticides in the water column, the ponds may favour their degradation and thus their elimination via numerous processes [28,29]. Ponds are composed of several compartments such as water column, vegetation, and bottom sediments where microorganisms, invertebrates and some vertebrates are living [30]. Each compartment of the pond is then positioned to play a role in the different processes of degradation, transformation, transfer and storage of pesticides [31,32].

Many physicochemical processes take place in this type of wetlands, which modulate the fate of organic contaminants [33,34]. Accumulation in plants [35] and biofilms [36] and sedimentation process are the main method of pesticide storage in water reservoirs [37]. Such processes have been reported [38] to be essential in dissipating pesticides. Nevertheless, the sedimentation process depends first on the texture of transported particles (gravels, sands, silts, clays), properties of which can also influence the pesticide sorption [16,39–41]. Moreover, the rate of particle sedimentation depends on the particle size, which results in a wide range of spatial deposition [42].

Unlike metal contaminants, little is known about the controlling factors involved in the storage and dissipation processes of organic contaminants in an agricultural context. Many questions remain about mechanisms involved in pesticide fate and more generally about chemical and ecological quality of watercourses, since the longer a molecule remains stored in a compartment, the more likely that microorganisms or photolysis may degrade it [43,44]. Consequently, such a process is supposed to decrease the pesticide concentration and, by extension, its toxic effect.

In this context, the PESTIPOND project (<https://pestipond.cnrs.fr/> accessed on 18 June 2021, Copyright© 2019 ANR PESTIPOND) [45] aims to characterize the role of ponds in the mechanisms of storage/degradation of pesticides, and on their transfer in three different agricultural critical zones in France. One of them, the Bassioué Pond (BP), is located in the Montoussé catchment at Auradé (Gers) in the south-western part of France [22,46,47]. Based on current knowledge in the literature, we investigated how pesticides were retained in the BP in order to fill some gaps of the fate of pesticides in wetlands. With reference to the cultivated crops in agricultural catchments, the behaviour of six pesticides chosen for their different $\log K_{OW}$ (metolachlor, boscalid, epoxyconazole, tebuconazole, aclonifen and pendimethalin) was investigated. Considering their different physicochemical properties, it can be hypothesised that they are not stored or degraded in the same way or in the same compartments [44].

The objectives of this study were: (i) to quantify the pesticide concentrations in the pond water and sediments, (ii) to characterise their spatial distribution and their partitioning from one compartment to another; (iii) to link their occurrence to the upstream catchment land cover and agricultural practices; (iv) to identify the key physico-chemical parameters which explain their presence and their distribution in water and sediment; (v) and to highlight the main controlling factors of pesticide behaviour within the pond, such as sediment texture or sediment depth.

2. Materials and Methods

2.1. Study Site

The Bassioué Pond (BP) is located in the Montoussé catchment (320 ha) at Auradé (Gers, France) [22,46,47] (Figure 1A–C). The Montoussé stream joins the Boulouze river, a right tributary of the Save river which flows into the Garonne river (the largest river in the

South-West France) on its left bank. This agricultural catchment, laying on carbonate-clayey molasse deposits with calcareous soils, is mainly cultivated with 90% of the surface area covered by wheat, sunflower, colza crops in a two-year rotation. The fertilisers, mainly of NPK type, are applied from January to April [48] and the pesticides are mainly spread during the spring period (April–May). Mainly, herbicides and insecticides are concerned with preventing diseases and adventive weeds [49]. The soils are mainly silty-clayey [46] and undergo significant erosion process because of steep slopes, tillage and significant storm events in spring [1,2,50]. This has led to very shallow soils at the tops of the hills (20–50 cm) and deeper alluvial and colluvial soils, which can reach more than 2.5 m downslope [46] in the stream valleys.

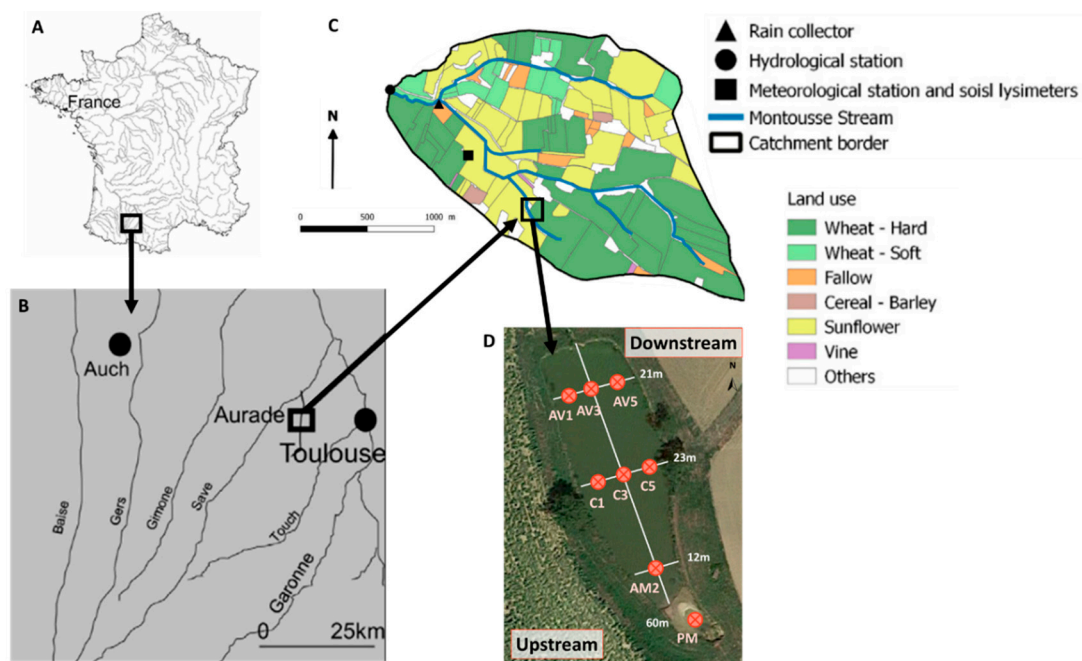


Figure 1. Location of the field study site at: (A) the country scale, (B) the Garonne basin scale, (C) the Auradé catchment scale with the mean land cover in 2008–2009, as an example, since the land is occupied on a yearly rotation, and (D) the pond scale (satellite image from Google map, <https://www.google.fr/maps/> accessed on 18 June 2021, Images ©2020 CNES/Airbus, Landsat, Maxar Technologies, Données cartographiques ©2020, France) with the sampling points common for both sampling campaigns (A–C adapted from Ponnou-Delaffon et al. [47]).

The BP is located in the upper part of this catchment ($1^{\circ}04'38.1''$ E, $43^{\circ}33'04.7''$ N) and its drainage sub-catchment represents an area of 28 ha (Figure 1C). This pond was set up in 1970 for recreation and was dragged in 2015 for the last time [51]. BP is 60 m long, 21 m large (in the middle part) and the surface area is 971 m² (for the entire pond system). The pond depth reaches 3 m in downstream parts but currently the water depth is only between 30 and 50 cm. Indeed, the pond has been filled by a huge amount of sediments eroded from the cultivated soils upstream and transported by several consecutive storm events, particularly between 2016 and 2018 [51]. In spring 2018, a major erosive flood event [47] fashioned a sediment clump (5 m long, 7 m large) in the very upstream part of BP (between PM and AM2 points, see Figure 1D). This created a small, very shallow secondary pond of 7.5 m long and 5 m large, which communicates with the major pond, except when the inlet water drainage is limited (Figure 1). On the sediment clump, a shrubby vegetation began to develop very dynamically in spring 2019 (Figure 1), and constitutes the main vegetation area in the pond.

2.2. Field Sampling

Two sampling campaigns of water column and bottom sediment, the two main compartments, were carried out on contrasted seasons in November 2019 and July 2020. During the first campaign performed on 18 November 2019, water samples were collected upstream and downstream of the pond and in the middle of the pond (corresponding to point C3, see Figure 1). The entire pond was first gridded according to the distances shown in Figure S1, which allowed for the selection of a total of 22 sampling points for sediments following a regular quadrat throughout the pond. This allowed the most exhaustive spatialized knowledge considering the size and the shape of the pond. Based on the results of the first campaign, eight points of interest were selected for the second sampling campaign (Figure 1C).

Sediments were sampled from a boat using a corer (UWITEC) with 8.8 cm diameter plexiglass tubes. The cores were carefully transported to the pond bank and treated immediately after a few minutes of rest, if necessary, to allow sedimentation of the particles resuspended during the operation.

The water collected at the top of the sediment core using a syringe was divided into two stored aliquots; one was dedicated to the measurement of the physicochemical parameters (only for the second campaign, Section 2.3.1) in polyethylene bottles and a second was for pesticide analysis in the dissolved fraction (Section 2.3.2) in glass bottles.

Sediment samples were then collected at different depths of the core: at the surface (0–2 cm) for autumn and summer campaigns respectively called Aut-S and Sum-S, and in the middle (2–12 cm) and at the bottom (12–17 cm) for the summer campaign, called Sum-M and Sum-D. For all sediment samples, organic carbon and nitrogen contents and the micro-granulometry (Section 2.4.2) were performed, whereas pesticide concentrations were measured for surface samples on the eight common points to both campaigns (Section 2.5) and deep samples for the second campaign.

2.3. Pre-Treatment and Analysis of Water Samples

2.3.1. Physico-Chemical Parameters

Water samples were first filtrated on acetate cellulose filters (\varnothing : 47 mm, pores size: 0.2 μm , Whatman, Maidstone, UK) previously weighed and rinsed with ultrapure water in order to avoid any contamination. Then the filtrate was collected and separated into four aliquots. One aliquot of 20 mL was dedicated to dissolved organic carbon (DOC) analysis, performed with a TOC-meter (Shimadzu TOC 5000 analyzer, Shimadzu Corporation, Kyoto, Japan) using a catalytic oxidation with a 680 °C combustion and a CO_2 detection using a non-dispersive infrared gas analyzer (NDIR; ISO NF EN 1484). For this analysis, the quantification limit is 0.1 $\text{mg}\cdot\text{L}^{-1}$ of C. A second aliquot of 50 mL acidified with a few droplets of HNO_3 (concentration 6 N) was used for cation analysis (Ca^{2+} , Mg^{2+} , Na^+ , K^+) by ICP-OES (Iris Intrepid II XLD, Thermo Electron, Thermo Fisher Scientific, Waltham, MA, USA, NF EN ISO 14911) with a limit of detection between 5.3 and 40 $\text{g}\cdot\text{kg}^{-1}$. A third aliquot of 1.5 mL was prepared for anion analysis (Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^-) performed with a liquid chromatography coupled with an UV-visible detector (Dionex Chromatograph ICS 5000+, Thermo Fisher Scientific, Waltham, MA, USA, T90-046–NF EN ISO 10304-2, September 1996). The detection limit for anions is between 0.2 and 65 $\mu\text{mol}\cdot\text{L}^{-1}$ depending on the element. Finally, a fourth aliquot of 50 mL was dedicated to alkalinity analysis, which was performed by hydrochloric acid titration (HCl 0.02 N and a Metrohm titrant, 716 DMS Titrino, Metrohm, Riverview, FL, USA; NF EN ISO 9963-1) with a limit of detection at 30 μmol of HCO_3^- . Secondly, the suspended matter collected on the filter was dried for 24 h in an oven at 40 °C, and weighed once more in order to obtain the dry weight.

2.3.2. Pesticide Quantification

Six pesticides were targeted for quantification: metolachlor, aclonifen, tebuconazole, pendimethalin, boscalid and epoxyconazole. For this purpose, two stock solutions

of six deuterated internal standards (metolachlor D6, aclonifen D5, tebuconazole D6, pendimethalin D5, boscalid D4, epoxiconazole D4; Cluzeau Info Labo C.I.L.) were prepared at a final concentration of 20 and 80 $\mu\text{g}\cdot\text{L}^{-1}$ in methanol (purity: 99.8%, ACROS organics). A third stock solution was prepared with the pesticide standards at a final concentration of 100 $\mu\text{g}\cdot\text{L}^{-1}$ in methanol for the establishment of the calibration curve. In the study, only three molecules were considered: boscalid, tebuconazole and metolachlor, in regard to their effective use by the farmers and to their chemical characteristics (see Table S1 for the data relative to the three other molecules).

Aliquots of 500 mL of raw water from the surface of the water column and the interface with sediments were filtrated with a GF/F filter (\varnothing : 45 mm, pore size: 0.7 μm , glass fiber, WhatmanTM, Maidstone, UK). A volume of 19 mL of the filtrate was then collected and introduced in an amber glass bottle along with 100 μL of internal standards at a concentration of 20 $\mu\text{g}\cdot\text{L}^{-1}$. The filter was cut into 16 pieces and added in a 50 mL tube with 10 mL of methanol and 100 μL of internal standards at a concentration of 80 $\mu\text{g}\cdot\text{L}^{-1}$. The tube was vortexed for 30 min at 1250 RPM and then centrifugated at 4 $^{\circ}\text{C}$ for 25 min at 6000 RPM. Then 2 mL of the supernatant was collected and placed into an amber glass bottle previously filled with 17 mL of ultrapure water (MilliQ).

A SBSE (Stir Bar Sorptive Extraction) bar was introduced in the amber bottle which was then placed on a magnetic stirrer plate for agitation at 1000 RPM for 3 h. After agitation, the SBSE bar was taken away, rinsed with ultrapure water, dried and finally placed into a thermodesorption tube.

The thermodesorption tubes were placed on the GC-TD-MS/MS autosampler. For each sample, the thermodesorption was performed with a gradient of temperature ranging from 30 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ with a step of 60 $^{\circ}\text{C}$ per minute up to the maximum temperature, and then stabilized for 6 min. After this process, the sample was injected at a temperature of -10°C , then according to a temperature gradient ranging from -10°C to 280 $^{\circ}\text{C}$ (60 $^{\circ}\text{C}$ per minute step) and finally a 4-min step at 280 $^{\circ}\text{C}$.

Chromatographic separation was performed using a TRACE 1300 Gas Chromatograph. A fused-silica capillary column Thermo Scientific TraceGOLD TG-MS (30 m \times 0.25 mm i.d \times 0.25 μm film thickness of 5% phenyl, 95% poly-dimethylsiloxane) was used. The chromatographic part was coupled to a triple quadrupole mass spectrometer (TSQ 8000 EVO, Thermo Fischer Scientific, Waltham, MA, USA), a Thermal Desorption Unit (TDU), Cooled Injection System (CIS 4) and MultiPurpose Sampler (MPS) to introduce Twister bars into the TDU system (all GERSTEL). Molecules were detected using a Selected Reaction Monitoring (SRM) mode, in Electron Impact (EI) mode at 70 eV. Finally, the quantification of pesticides was possible thanks to internal calibration. The detection limit is about 0.1 $\text{ng}\cdot\text{L}^{-1}$. Data reprocessing was done with TraceFinder software (Thermo Scientific version 3.3).

2.4. Pre-Treatment and Analysis of Sediment Samples

2.4.1. Pre-Treatment of the Sediments

On the day of sampling, the sediments were placed directly in glass dishes to dry up for two weeks at room temperature. After this period, they were disaggregated in an agate mortar with a pestle, avoiding crushing the grains. Samples were homogenized and passed through a metal sieve with 2 mm mesh for micro-granulometry analysis of the total fraction. The finest fractions, sieved at 63 μm , were used to analyse the physico-chemical parameters and the pesticides, considering its higher abundance in sediment as well as its high adsorption capacity of pesticides [52]. This procedure also allowed normalizing the different sediment samples, which can have different grain size distributions.

2.4.2. Texture and Micro-Granulometry

The micro-granulometry of the sediments was performed in order to characterize the grain size distribution of each samples and their texture, and to determine the contribution of the different fractions: 0–2 μm (clays), 2–20 μm (fine silts), 20–63 μm (coarse silts),

63–200 μm (sands) and 200 μm –2 mm (gravels). The micro-granulometry was determined by wet laser diffraction (LA920-V2 Horiba ISO 13320) with a detection limit comprises between 10 nm and 3.5 mm.

2.4.3. Organic Carbon and Nitrogen Analysis

Prior to analysis, the samples were first decarbonated because of the high carbonate content in the sediments. About 0.5 g of the finest fractions ($<63 \mu\text{m}$) was decarbonated by alternating the addition of a few drops of hydrochloric acid and then dried on a hot plate at 40°C until the disappearance of the effervescence. Then, the sample was rinsed with ultrapure water and dried again before analysis by gas chromatography couple with a TCD detector (Flash2000 Thermo Scientific, NF ISO 10694; NF ISO 13878; NF EN 13137, 1995). The detection limit is 200 ng.

2.5. Pesticide Analysis

A mass of 0.5 g of the finest fraction ($<63 \mu\text{m}$) of the sediment was placed in a 50 mL tube with 10 mL of methanol and 100 μL of internal standard at a concentration of $80 \mu\text{g}\cdot\text{L}^{-1}$ (as described in Section 2.3.2). Then the sample was vortexed for 5 min at 1200 RPM, placed in ultrasound (50–60 Hz, Fisher ScientificTM, Illkirch, France) for 30 min, and vortexed again for 5 min at 1200 RPM. Finally, the sample was centrifugated at 4°C for 25 min at 6000 RPM. Two mL of supernatant was collected and placed in an amber glass bottle with 17 mL of ultra-pure water. Pesticides were quantified by GC-MS/MS as described for water samples (see Section 2.3.2).

2.6. Data Processing

A Kruskal-Wallis test was performed on the pesticide concentration in water at the interface and the surface sediment between the two different seasons. It was considered significant at a p -value of less than 0.05. Statistical data treatment such as correlations (using Spearman correlation due to non-normal distribution of the data) was performed using R Studio software (version 3.6.1) with the following packages: corrplot, gclus, Hmisc and PerformanceAnalytics.

The spatialized map of the texture and pesticide concentration in the pond sediments was created on ArcGis software (ArcMap, version 10.5). An interpolation of sediment texture (in percentage of total) was done for the autumn campaign, during which the sampling points were maximum. The pesticide concentrations were then represented for each sampling point on the same map.

The partition coefficient of pesticide concentration $[C]$ between sediment and water (K_d) was calculated as follows [53]:

$$K_d = \frac{[C]_{\text{sediment}}}{[C]_{\text{water}}} \quad (1)$$

where K_d is expressed in $\text{L}\cdot\text{g}^{-1}$, pesticide concentration in sediment and in water in $\mu\text{g}\cdot\text{g}^{-1}$ and in $\mu\text{g}\cdot\text{L}^{-1}$, respectively.

The K_{OC} , which represents the molecule ability to sorb onto the organic matter, was then determined as follows:

$$K_{OC} = \frac{K_d}{\text{POC}} \quad (2)$$

where K_{OC} is expressed in $\text{L}\cdot\text{g}^{-1}$ and the particulate organic carbon (POC) in $\text{g}\cdot\text{g}^{-1}$.

3. Results

3.1. Chemical Composition of Water and Sediment

The physico-chemical conditions measured in the pond water column were similar during the two field campaigns, except for a slight decrease in the water height and water temperature twice higher in summer (Table 1A).

Table 1. In-situ physico-chemical conditions, (A) Water column and (B) and (C) Sediment compartment: mean, standard deviation, minimal and maximal value (Aut: autumn, Sum: summer) for two core depths (S: surface, D: deep). Clays: 0–2 μm ; fine silts: 2–63 μm ; coarse silts: 63–200 μm ; sands: 200 μm –2 mm; gravels: >2 mm, * represents significant differences for pesticide concentrations between summer and autumn.

(A)																					
Water	Water Height cm		pH		Conductivity $\mu\text{S}\cdot\text{cm}^{-1}$		T °C		O_2 $\text{mg}\cdot\text{L}^{-1}$		DOC $\text{mg}\cdot\text{L}^{-1}$		[metolachlor] $\text{ng}\cdot\text{L}^{-1}$		[tebuconazole] $\text{ng}\cdot\text{L}^{-1}$		[boscalid] $\text{ng}\cdot\text{L}^{-1}$				
Season	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	
Mean	46.4	36.3	7.7	7.8	794.0	703.3	9.3	20.5	8.5	7.4	4.7	4.7	5.6 *	9.9 *	8.8 *	49.3 *	43.6	42.8			
sd	1.2	2.6	0.1	0.1	23.8	0.3	0.5	0.3	1.7	1.6	0.4	0.2	0.4	0.6	0.9	10.4	0.8	9.6			
min	30.0	30.0	7.6	7.7	751.0	703.0	8.8	20.1	5.2	4.5	4.1	3.4	4.9	8.0	6.8	18.4	42.1	15.1			
max	50.0	50.0	7.9	8.0	833.0	704.0	10.2	21.1	10.9	10.0	5.4	5.1	6.8	10.7	11.0	62.7	45.7	58.1			
(B)																					
Sediments	POC $\text{mg}\cdot\text{g}^{-1}$		C/N		Clays %		Fine silts %		Coarse silts %		Sands %		Gravels %								
Season– Core depth	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D
Mean	11.4	10.9	9.0	5.4	6.5	5.9	13.2	11.5	17.2	70.8	76.0	60.4	10.8	8.4	7.7	5.0	3.1	4.8	0.2	1.0	9.8
sd	0.4	0.6	0.3	0.2	0.2	0.1	1.1	0.8	2.0	3.4	2.5	6.5	2.0	2.0	0.8	1.9	1.0	1.2	0.1	0.4	9.0
min	9.8	7.6	6.8	4.8	6.0	5.5	9.4	7.6	3.2	57.3	65.1	15.9	5.2	3.8	3.2	0.4	0.2	1.8	0.0	0.0	0.1
max	13.1	12.3	10.2	6.4	7.8	6.3	17.1	14.7	20.9	80.9	82.4	71.3	17.7	17.5	10.6	14.6	7.2	12.5	0.8	3.2	72.8
(C)																					
Sediments	[metolachlor] ($\mu\text{g}\cdot\text{kg}^{-1}$)			[tebuconazole] ($\mu\text{g}\cdot\text{kg}^{-1}$)			[boscalid] ($\mu\text{g}\cdot\text{kg}^{-1}$)			$K_{\text{d met}}$ ($\text{L}\cdot\text{g}^{-1}$)		$K_{\text{d tebu}}$ ($\text{L}\cdot\text{g}^{-1}$)		$K_{\text{d bosc}}$ ($\text{L}\cdot\text{g}^{-1}$)		$K_{\text{oc met}}$ ($\text{L}\cdot\text{g}^{-1}$)		$K_{\text{oc tebu}}$ ($\text{L}\cdot\text{g}^{-1}$)		$K_{\text{oc bosc}}$ ($\text{L}\cdot\text{g}^{-1}$)	
Season– Core depth	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut-S	Sum-S	Sum-D	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum
Mean	2.6 *	1.3 *	3.6	8.1 *	21.7 *	8.3	5.5 *	3.3 *	10.8	0.48	0.21	0.94	0.20	0.13	0.16	48.8	18.8	96.1	18.8	12.8	16.9
sd	0.3	0.1	0.5	0.6	2.6	1.0	0.4	0.1	1.3	0.05	0.05	0.06	0.05	0.01	0.04	7.8	4.1	14.0	4.8	1.8	5.7
min	1.9	0.6	0.7	5.9	7.4	2.3	4.3	2.7	6.9	0.28	0.06	0.70	0.04	0.11	0.07	24.0	8.3	60.0	5.6	9.9	5.9
max	3.8	1.7	5.4	11.3	28.1	11.3	7.7	3.5	8.7	0.61	0.51	1.11	0.41	0.15	0.41	81.1	43.9	160.9	43.6	21.6	54.0

The particulate organic carbon (POC) content and the C/N ratio in sediments were similar whatever the season or the depth (Table 1B). As measured in 10 ponds in the same area by Wu and Probst [27], sediments were highly carbonated (Ca values averaging $71 \text{ mg}\cdot\text{g}^{-1}$), with Al, Mg, Fe and Mn as other major elements.

In this study, six pesticides were targeted and detected in both compartments (see Table S1).

However, only the results for three of them are presented and discussed because of their occurrence and relevance with regard to their chemical properties. Indeed, concentration in sediment for aclonifen and pendimethalin did not exceed $1.1 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$, and ranged between 1.5 and $4.3 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ for epoxiconazole, whose $\log K_{OW}$ of 3.4 is in between those of metolachlor and tebuconazole (for details, see Table S1).

The pesticide concentrations in water and sediments ranged between 4.9 to $10.7 \text{ ng}\cdot\text{L}^{-1}$ and 0.6 to $5.4 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ for metolachlor, 15.1 to $58.1 \text{ ng}\cdot\text{L}^{-1}$ and 2.7 to $8.7 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ for boscalid and 6.8 to $62.7 \text{ ng}\cdot\text{L}^{-1}$ and 2.3 to $28.1 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ for tebuconazole, respectively (Table 1A,C). The pesticide concentrations were rather low in both compartments. The tebuconazole and metolachlor concentrations in the pond water column are, respectively, 5 and 20 times lower than those measured some years ago during flood events in the Save river draining the same areas [16]. The pesticide concentrations in sediments were moderate compared to some other sites: metolachlor concentrations between 40 and $210 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ were measured in a large reservoir upstream Toulouse city on the Garonne river (only partly draining an agricultural area, SW France) [54]; several hundred g per kg of boscalid were observed in the Mediterranean area [55] and about $45 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ in an agricultural area in the United States [56].

The seasonal trends of pesticide concentrations were not similar in the two compartments. In the water column, the concentrations were significantly higher in summer than in autumn (Table 1A), except for boscalid for which concentrations were in the same range. In the bottom sediments, boscalid and metolachlor concentrations were around two times higher in autumn than in summer, and inversely for tebuconazole (Table 1C). Moreover, an increase in concentration was observed with depth in summer (around three times higher), except for tebuconazole which had similar concentrations in both seasons at the sediment surface.

The average K_d ratio (see Section 2.5) varied between 0.2 and $0.94 \text{ L}\cdot\text{g}^{-1}$ (minimum 0.06, maximum $1.11 \text{ L}\cdot\text{g}^{-1}$, Table 1C) according to the pesticide molecule. It was between two and five times higher in autumn than in summer, except for boscalid for which it was stable (Figure 2). For tebuconazole and metolachlor, K_d increased in summer from upstream to downstream for the three points in the main pond (except “PM”), however this was not observed in autumn. Values higher than 1 can be found in other studies, for ex. 1.7 – $34 \text{ L}\cdot\text{g}^{-1}$ for insecticides in wetlands [57]. This is not surprising since K_d varies in time and space, and so cannot be defined as immutable for a molecule [18].

The calculated average K_{OC} ranged between 12.8 and $96.1 \text{ L}\cdot\text{g}^{-1}$ (minimum $5.6 \text{ L}\cdot\text{g}^{-1}$, maximum $160.9 \text{ L}\cdot\text{g}^{-1}$, Table 1C) according to the pesticide molecule. As for K_d , the K_{OC} decreased strongly from autumn to summer for metolachlor and tebuconazole (Figure 2). For the three considered molecules, the K_{OC} decreased from upstream to downstream in autumn (if we except “PM”). This is consistent since the K_{OC} is dependent on sediment POC content which was constant from upstream to downstream and on the pesticide considered [58] and was determined from the K_d (Equations (1) and (2)).

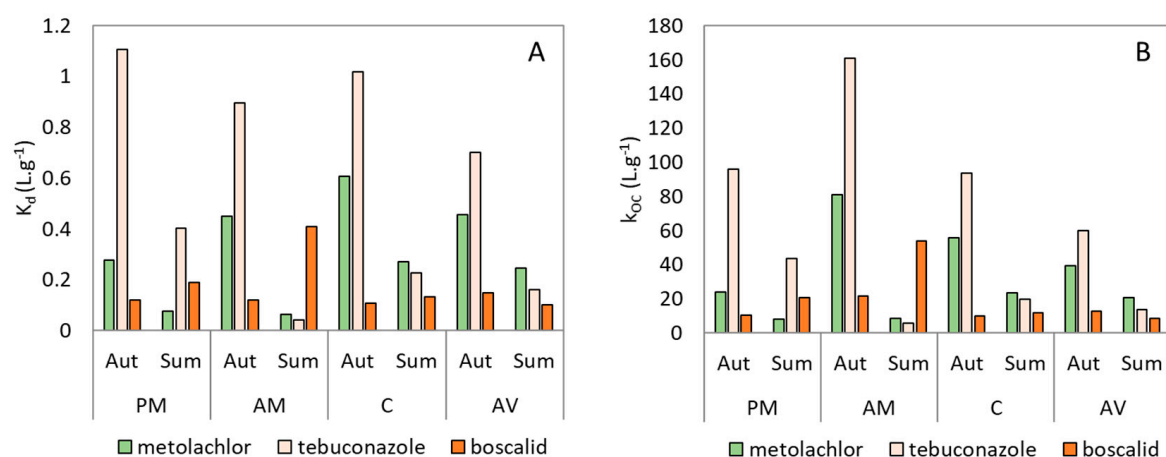


Figure 2. K_d partition coefficient (A) and K_{oc} organic carbon/water distribution coefficient (B) for three pesticide molecules measured in surface sediments, according to the seasons (Aut: autumn 2019 and Sum: summer 2020) and the localization in pond (sampling points PM, AM, C and AV, see Figure 1).

3.2. Sediment Texture

For the two sampling campaigns, fine silts (2–20 μm) were dominating the texture of the <2 mm sediment fraction. These fine silts represent on average more than 70% in surface sediment and 60% in deep sediment (Table 1B; Figure 3). The exception was for PM, the upstream sampling point (Figure 1) where the main fraction was sand during the summer campaign (Figure 3).

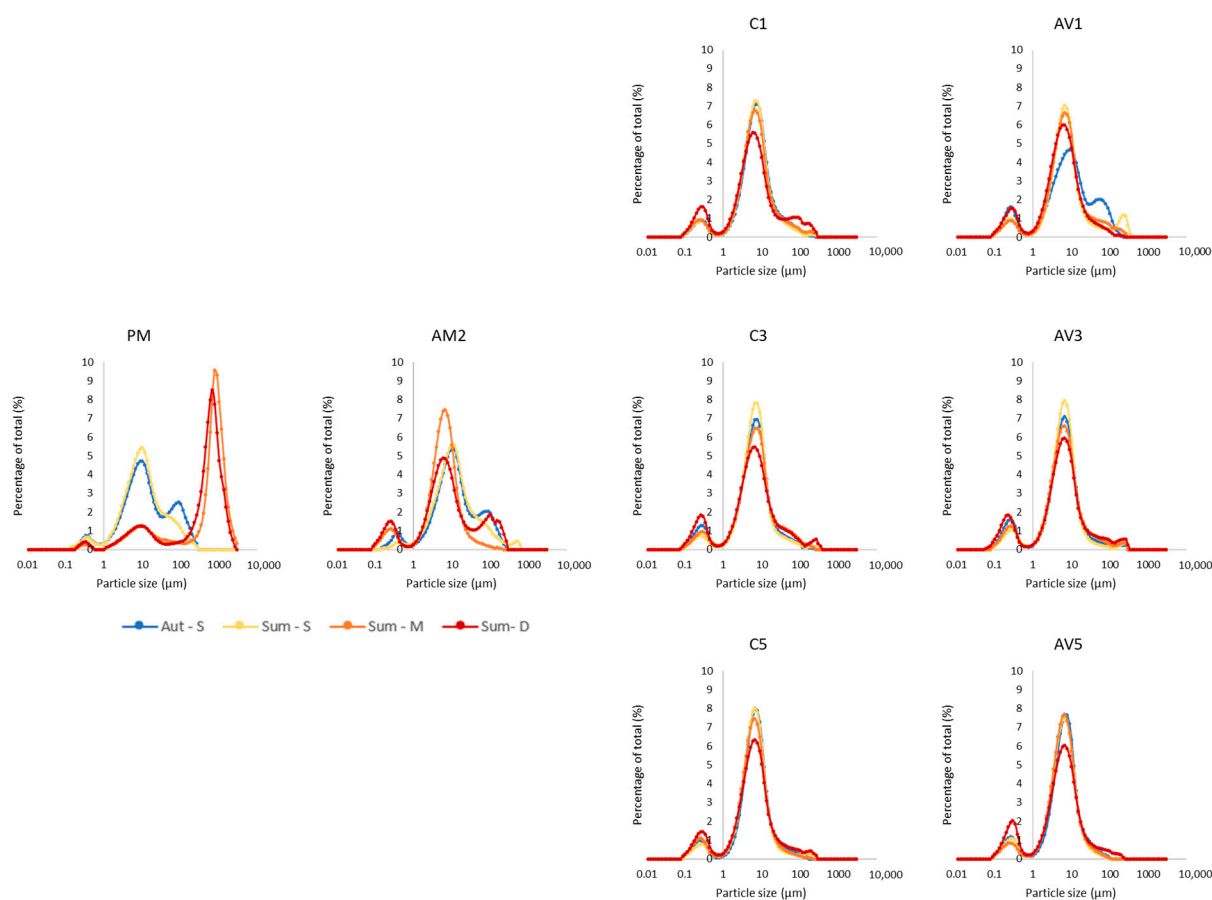


Figure 3. Texture of the pond sediments collected during the different seasons and depths: grain size distributions in % of the total fraction (<2 mm) for the different sampling points (PM to AV5, see their location in Figure 1).

For all sampling points, the grain size distribution of the sediment (from 0 to 2 mm) showed three peaks: (i) a first one between 0.25 and 0.35 μm (1–2% of the total fraction) corresponded to the finest clays; (ii) a second major one between 6.5 and 8.5 μm (representing 4.6–7.8% of the total sediment) was for the fine silts, except PM point (the peak did not exceed 2%); (iii) a third peak represented the coarse particles (such as fine sands), and which intensity depended on the location in the pond. It was very weak between 0.2 to 1% for C1–C5, AV3 and slightly higher (up to 2%) for AV5 and AM2 and AV1. This peak was the major one in PM sampling point (see Figure 3).

An increase in the fine silt fraction was noticeable from upstream to downstream regardless of the season or the depth considered, with outlier patterns for AV1 and PM, as mentioned above.

The patterns for the surface sediments were overall similar between the two seasons, although clays were slightly higher in autumn than in summer. The reverse was true for the fine silts. For deeper samples, with the exception of the sampling points at the inlet of the pond (PM, AM2), a depth gradient of intensity was visible for the main peak, i.e., surface > middle > bottom. This gradient was reversed for the first peak of clays.

3.3. Relationship between Pesticide Concentrations and Physico-Chemical Parameters

A correlation matrix was carried out with all the parameters measured on the Aut-S, Sum-S and Sum-D samples (Figure 4A–C, respectively) for all the campaigns and sample type. A significant positive correlation was highlighted between the distance (distance from upstream, the point PM = 0, AM = 10 m, C = 30 m, AV = 50 m) and the percentage of clays and fine silts, and conversely, a negative correlation with gravel. As a whole, the pesticide concentrations were significantly related to the sediment texture.

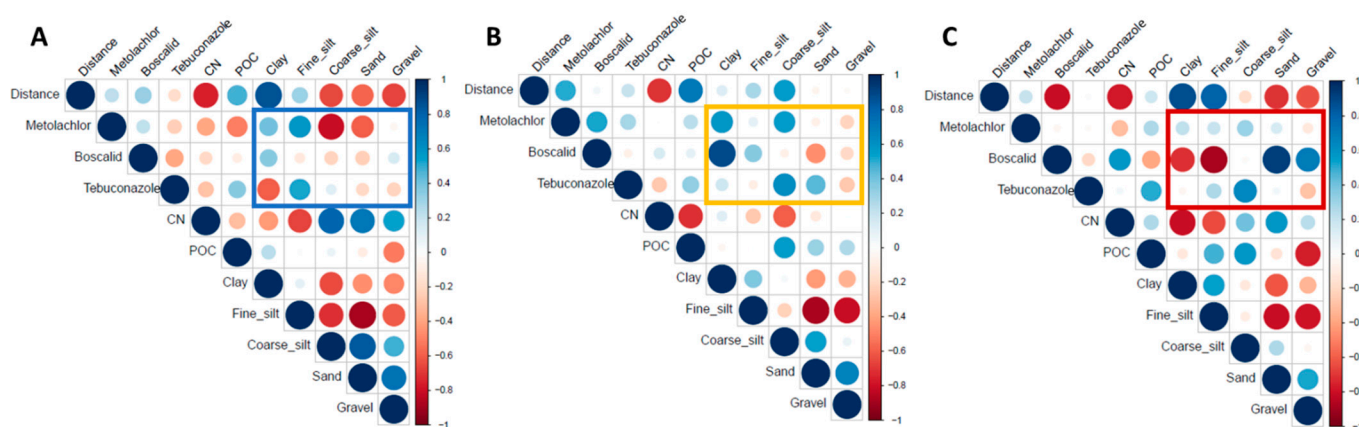


Figure 4. Correlation matrix for all the parameters measured in the sediment samples from (A) Autumn campaign/Surface sediment, (B) Summer campaign/Surface sediment and (C) Summer campaign/Deep sediment. Color and size of circles represent the correlation strength (Spearman's rho coefficient r_s , $n = 8$); blue and red mean positive and negative values, respectively. The r_s values outlined by rectangles refer to the relationships between pesticide content and sediment texture. r_s values and their significance were given in Supplementary Materials (Figures S2–S4).

The pesticides' concentrations were not significantly related to the physico-chemical parameters in sediments collected in autumn. Nevertheless, in autumn at the sediment surface, metolachlor was strongly positively related to the fine fractions, and negatively to the coarser ones ($r_s = -0.81$, p -value < 0.05, $n = 8$, Figure S2). The correlations between tebuconazole concentration and sediment grain size were not significant but they were positively ($r_s = 0.52$ and $n = 8$) and negatively ($r_s = -0.6$ and $n = 8$) related to fine silts and to clays, respectively (Figure 4A). In summer at the sediment surface, boscalid and metolachlor concentration were positively related to clay content (Figure 4B; $r_s = 0.89$ and $r_s = 0.57$; p -value < 0.01, $n = 8$, respectively, Figure S3), while at deep sediment in autumn,

it was the reverse for boscalid (Figure 4C, $r_s = 0.93$ with sand; p -value < 0.01 and $r_s = 0.71$ with clays and $r_s = -0.88$; p -value < 0.05 with silts Figure S4).

For surface sediments, no significant relationship was identified between pesticide concentrations and POC content or C/N ratio (Figure 4A,B), except non-significant positive and negative correlations between tebuconazole or metolachlor and POC ($r_{s \text{ aut-S}} = 0.36$, $r_{s \text{ Sum-S}} = 0.33$, $r_{s \text{ Aut-S}} = -0.50$, Figures S2 and S3). In deeper sediment, non-significant positive relationships were observed between boscalid content and C/N ($r_s = 0.57$, Figure 4C), and between tebuconazole and POC ($r_s = 0.50$, Figure S4).

3.4. Spatial Distribution of Sediment Texture and Pesticide Concentration

The grain size distribution data of the sediments collected at the 22 sampling points (Figure S1) were used to performed interpolation maps of the sediment texture distribution (Figure 5). They evidenced a general trend going from upstream to downstream, with the coarser fractions in the upper part of the pond and a higher percentage of fine particles (clays and fine silts) in the lower part (more details Table S2). These interpolation maps were then used to illustrate the overlapping distribution of pesticide concentrations in the sediment samples collected at the 14 sites.

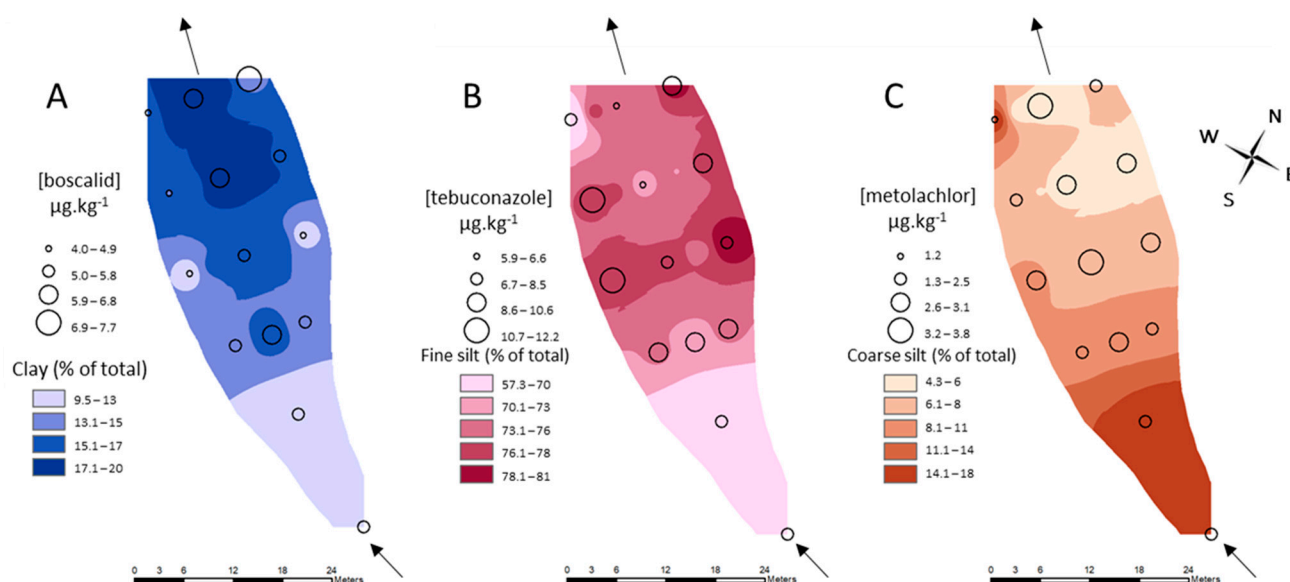


Figure 5. Pond maps of spatial interpolation for grain size distribution compared with pesticide concentration during the autumn campaign. (A) clay percentage and boscalid concentration, (B) fine silt percentage and tebuconazole concentration, (C) coarse silt percentage and metolachlor concentration. For each granulometric fraction, the map results from a spatial interpolation of the sampling point measurements ($n = 22$ points) using ArcGis software. Arrows indicate the flow direction.

During the autumn period, the distribution of the sediment grain size and pesticide concentration depended on the location in the pond from upstream to downstream (Figures 3 and 5 and details Table S1). On Figure 5A, boscalid concentrations were higher in the centre and downstream parts of the pond. Higher boscalid concentration in sediment can be related to the higher clay content, which increased from upstream to downstream.

The spatial distribution of the fine silts indicated a higher relative proportion in the middle and the down boarder parts of the pond (Figure 5B). Except one point on the eastern middle boarder of the pond (C5, Figure 1), the highest concentrations of tebuconazole could be related with the highest fine silt content observed in these areas. Finally, Figure 5C evidenced the highest proportion of coarse silts distributed in the upstream part of the pond, as well as locally at AV1 (downstream on the left bank; Figure 5C). Metolachlor concentration, exhibited an inverse pattern with increasing percentage of coarse silt fractions from upstream to downstream and a lower value in AV1.

4. Discussion

4.1. Pesticide Origin and Seasonal Effect

The three most concentrated pesticide molecules were metolachlor, boscalid and tebuconazole (Table S1), particularly in sediments. These pesticides have contrasted physico-chemical properties. Indeed, metolachlor and boscalid have a similar hydrophilicity ($\log K_{OW} = 2.9$ and 3 , respectively), while tebuconazole is more hydrophobic ($\log K_{OW} = 3.7$), which makes it more likely to be retained by the sediments [32,59]. This property explains the higher K_d and K_{OC} values for tebuconazole than for the two other molecules (Figure 2).

These three pesticides have been used for decades in the Auradé catchment for crop protection and they are currently still allowed. Fungicides such as tebuconazole and boscalid were mainly used to limit the diseases on wheat and rapeseed crops, while herbicide metolachlor was used as a weed killer. Their direct spreading during the crop treatments and the burying of straws contribute to their accumulation in the soils located upstream the pond. Then, the erosion and soil leaching processes during storm events—particularly when soil cover is scarce in spring during the spreading period—contribute to the transfer into the pond of dissolved and particulate pesticides by surface and subsurface runoffs [16]. Then, the suspended particles with their associated pesticide molecules feed the sedimentation in the pond [27].

Consistent with agricultural practices for many years, the annual rotation of crops was observed during the two coring campaigns: sunflower in 2019 and wheat in 2020. Among the molecules of interest, metolachlor was applied in 2019 and tebuconazole and boscalid in 2020 to the respective crops. Their application in spring (April–May) might explain their dominance in the pond water column during summer compared with autumn (except for boscalid, which is similar for the two seasons). This seasonality effect is also visible in the bottom sediments for tebuconazole, which concentrations in core surface are twice as high in summer as in autumn (Figure 6A). This can be explained on one hand by its use by the farmers in spring and on the other hand by its transport by the major flood events, very erosive, occurring in May–June after the spreading period [52,53]. The decrease in concentration for this molecule observed both in the water column and in the sediments at the late autumn campaign can be related to a dilution effect by increasing discharge at this period, but also by its high rate of photo-degradability [60] and bio-degradability by vegetation [61] and biofilms [55]. Kalogridi et al. [14] observed the same effect linked to seasonality, even more obvious in water column than in sediment, in accordance with the surrounding crop and the relative pesticide treatment.

The lower significant concentration of metolachlor in summer 2020 compared with autumn 2019 (Table 1C, p -value < 0.05) was consistent with an absence of application on the crops in the upstream catchment in 2020. However, a dissipation of this molecule could also be assumed, through biodegradation by microorganisms. Indeed, C/N values below 8 (Table 1) indicate the contribution of a biological activity in the pond due to the presence of phytoplankton which favours the mineralization process [62]. Metolachlor was thus biodegraded gradually over time, and the low concentrations measured in summer 2020 compared to the literature values [54] might be related to residues from the previous year.

In contrast, the concentration of boscalid (applied on crops in 2020) in the surface sediment were significantly higher in autumn than in summer (Figure 6B). Indeed, this molecule was also applied on crops in 2018. During this year 2018, exceptional floods events occurred in spring, to such an extent that a sediment clump was created at the entrance to the pond (Figure 1D). This resulted in a significant sediment stock enriched in boscalid originating from soil surface layers. Complemented with the inputs in 2020, the molecule was resilient in the sediments and its concentration was modulated by the different biogeochemical processes (biodegradation, resuspension, bioturbation, etc.) inherent to environmental conditions. Meanwhile, high tebuconazole concentration during the two sampling campaigns does not rule out this hypothesis. Indeed, similar retention rates were mentioned for boscalid and tebuconazole in sediments due to their low bioavailability limiting their biodegradation linked to their physico-chemical properties [38,63].

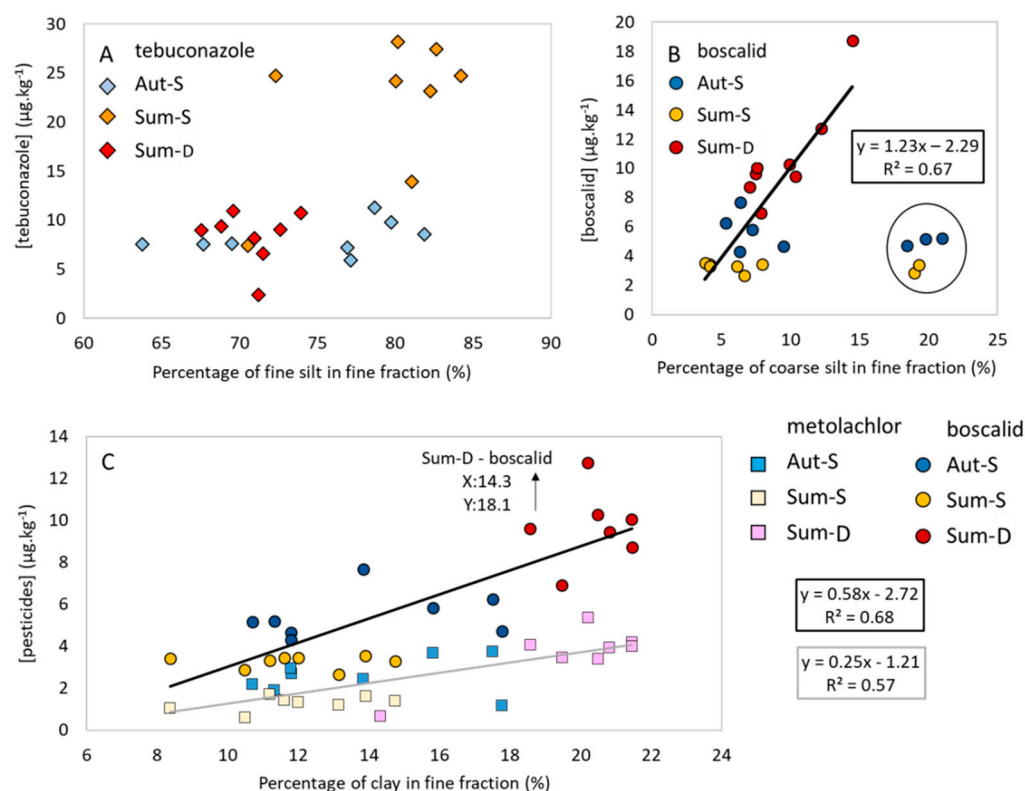


Figure 6. Relationships between pesticide concentration in sediments (in $\mu\text{g}\cdot\text{kg}^{-1}$) and the percentage of the different granulometric fine fractions for the different sampling seasons (Sum: summer; Aut: autumn) and depths (S: surface sediment; D: deep sediment). (A) tebuconazole *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. Factors Controlling Pesticide Concentration and Distribution

4.2.1. Sediment Texture

The results on grain size distribution highlighted the spatial variation of the sediment texture over the pond, with the dominance of coarser particles in the upper part and finer ones in the lower part of the pond. The opposite points in the pond, i.e., PM and AV1 (Figure 1), emphasized such substantial differences, i.e., a fairly marked proportion of coarser particles for PM (mainly in deep sediments). This difference in sedimentation was fully in line with the literature data, which mentioned that sediment texture varies with the location in ponds, the biggest particles settling much faster [37,42]. The interpolated maps evidenced a certain continuity in the process (Figure 5). The texture similarity at the entrance of the pond (between PM and AM2) indicated that there was no buffering effect of the sediment clump between these two sites. The anomaly to the general distribution pattern observed at the site AV1 (coarser fraction in the down part) on the left bank of the pond was linked to lateral runoff contribution from the lands of the nearby slopes. Indeed, the slopes in the area are steep and the flash flood events occurring when crops do not cover the soils directly contribute to soil erosion and transport of eroded particles to the stream and into the pond [7,8]. The dominance of clay and fine silts in sediments refers to the characteristics of the soils (clayey and silty) which cover this catchment and from which the pond sediments originate [46].

Sediment texture has already been considered as a key controlling factor for organic compound storage. Particularly, clay fraction is a powerful sorbent due to its large adsorption surface [41,64,65]. We confirm this statement with the significant relationship between

pesticide concentration and clay content in the sediments (Figures 4, 5 and 6C), especially for metolachlor and boscalid in the upper sediment layer. Boscalid concentration was however better controlled by clay fractions than metolachlor (Figures 4 and 6C), although these two molecules have a very similar $\log K_{OW}$ (2.9 for boscalid and 3 for metolachlor). This indicates that other physico-chemical properties of the molecules [53] and/or characteristics of the environment such as the water pH [66,67] or the carbonate content in the sediment [68] are also involved.

Another explanation could be the competition process between the molecules or other trace or major elements for adsorption onto the sediments [27,39]. Indeed, the high affinity of a molecule for the substrate in such carbonated conditions can rapidly inhibit the sorption ability for another. This is true whether it is a competition between organic contaminants or with other types of pollutants such as metals [39,65,66]. As an example, Xing et al. [69] showed a non-linear sorption phenomenon for metolachlor surrounded by other organic molecules. High oxide content in the sediments can also increase their specific surface area and can then play a major role on pesticide adsorption onto the sediments [27,70,71] as in this study. Depending on their physico-chemical properties, the pesticide molecules can be bound efficiently to oxides [71] as demonstrated with metamitron and iron oxides [70].

The sediment texture was a less significant controlling factor for tebuconazole, probably due to a multitude of factors, as presented before [66,68,71] masking or inhibiting this effect as observed by Gao et al. [72]. As mentioned above, sediments present a complex mineralogical composition [73]; potentially, they include a great amount of oxides which might induce favourable conditions for tebuconazole sorption in this compartment [74].

Surprisingly, boscalid was also associated to the coarser particles such as the coarse silts (coefficient of determination: $R^2_{bosc} = 0.67$, if we excluded the outliers PM, AM2 and AV1, Figure 6B) and to sands in deep sediments (Figure 4C, $r_s = 0.93$, p -value < 0.01, Figure S4). This suggests that this molecule was more persistent in sediments than the other ones. Because the organic matter content was very low, it could be assumed that the oxides present in the different granulometric fractions might be a key controlling factor of these molecules, as already mentioned for metals [27]. Moreover, the persistence of boscalid in wetland was demonstrated because this molecule adsorbs particularly well onto sediments, noticeably in carbonated conditions with high pH values [75]. Since it has a half-life of 246 days in soils, this adsorption process is not very reversible [75].

4.2.2. Sediment Depth

The pesticide concentrations measured in deep sediments were on average three times higher than in surface sediments. This was particularly obvious for boscalid and to a lesser extent, metolachlor (Figure 6B). In deep sediments, the physico-chemical conditions vary and influence the sediment capacity of pesticide sorption-desorption [76]. The pH [77], the redox potential [78], the clay content [76], the organic matter content [23] and the microbial biomass [79] are among the key parameters which can vary with the sediment depth and affect pesticide fate and concentration in the sediment column.

The pesticide concentration increase was consistent with the slight enrichment of clays in depth, probably due to the lixiviation process [80]. It was shown that clay and coarse silt fractions had some control over pesticide concentrations in the sediments (see Section 4.2.1).

Although the organic matter is considered as an important controlling factor of pesticide storage in sediments [18], no link between POC content and pesticide concentration could be demonstrated in the concerned pond. Indeed, the organic carbon content in the sediments was very low (around 1% and less), in the same order of magnitude as it is in soils [81] and there are few differences between POC content in sediment surface and in depth (10.9 ± 0.6 and 9.0 ± 0.6 mg·g⁻¹, respectively, Table 1B).

Other explanations remain possible for interpreting the vertical profiles of pesticide concentration in the sediments, such as carbonate level, which might contribute to some precipitation process as was evidenced for metals in various ponds in the area [27]. The

redox potential may influence the adsorption process in-depth, and favour conditions to higher concentration in the bottom of the core [82,83]. In addition, the impact of bioturbation might also be evoked as a modification of the redox condition [84,85]. In the field, significant macrofaunal activity related to bioturbation was observed. As explained by Katagi et al. [44], chemicals can be transported and distributed along the vertical profile of the sediments by bioturbation.

5. Conclusions

This study has highlighted the spatial distribution of pesticide concentration in a pond located in an agricultural catchment. Their occurrence according to the seasons of sampling depended on their use in the upstream catchment, on the discharge condition, namely on the occurrence of an erosive storm event, and on their biodegradability potential. The molecules of interest (metolachlor, tebuconazole and boscalid) were not accumulated in the same way in the pond bottom sediments in relation to their physico-chemical properties and to the environmental conditions. The sediment texture was one of the major controlling factors that could be highlighted. Although fine silts were dominant, our study confirmed that clays (here of smectite type) had a high sorption capacity for these organic molecules, meanwhile unexpectedly coarse silts participated to the control of boscalid. As molecules with a similar K_{OW} (2.9 for boscalid and 3 for metolachlor) behave differently with regard to the relationship with clay content, the influence of other physico-chemical parameters, such as pH/redox and mineralogical composition (carbonates, oxides) of the sediments, was suspected. Finally, these contaminants were retained and trapped over time in the deeper sediments, consistently with the increased clay content. A deeper insight is necessary to evaluate the influence of change in bio-physico-chemical conditions with depth and the biodegradation potential of these molecules. Finally, this study highlighted the capacity of these wetlands to trap pesticides in the sediments, and thus paves the way for new studies on the various processes taking place in this sediment compartment at surface and at depth.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w13131734/s1>, Figure S1: Dimensions of the Bassioué pond (map from Google map) and sampling points for the autumn campaign (November 2018), Table S1: Pesticide concentrations in $\mu\text{g.kg}^{-1}$ in the pond sediments for both campaigns (Autumn and summer), Table S2: Sediment physico-chemical characteristics, Figure S2: Correlation matrix (Spearman r_s) for parameters measured in the sediment samples collected during the autumn campaign at the surface. The upper triangular matrix shows the correlation strength with the significance levels (red stars): no star means not significant, * p -value < 0.05, ** p -value < 0.01, *** p -value < 0.001. Histograms are kernel density estimation. The lower triangular matrix is composed by the bivariate scatter plots with a fitted smooth line. The r_s outlined by the blue rectangle refer to the relationships between pesticide content and sediment texture, Figure S3: Correlation matrix (Spearman r_s) for parameters measured in the sediment samples collected during the summer campaign at the surface. The upper triangular matrix shows the correlation strength with the significance levels (red stars): no star means not significant, * p -value < 0.05, ** p -value < 0.01, *** p -value < 0.001. Histograms are kernel density estimation. The lower triangular matrix is composed by the bivariate scatter plots with a fitted smooth line. The r_s outlined by the blue rectangle refer to the relationships between pesticide content and sediment texture, Figure S4: Correlation matrix (Spearman r_s) for parameters measured in the sediment samples collected during the summer campaign at the depth. The upper triangular matrix shows the correlation strength with the significance levels (red stars): no star means not significant, * p -value < 0.05, ** p -value < 0.01, *** p -value < 0.001. Histograms are kernel distribution estimation. The lower triangular matrix is composed by the bivariate scatter plots with a fitted smooth line. The r_s outlined by the blue rectangle refer to the relationships between pesticide content and sediment texture.

Author Contributions: Conceptualization, B.C., A.P. and J.-L.P.; field experimentation: B.C., A.P., J.-L.P., T.C., V.P.-S. and F.G.; sample preparation, B.C., T.C. and P.E.; analysis, D.R. and Plateforme d'Analyses Physico-Chimiques; data curation, B.C.; writing—original draft preparation, B.C.;

writing—review and editing, A.P. and J.-L.P.; visualization, B.C.; supervision, A.P. and J.-L.P.; project administration and funding acquisition, A.P. and J.-L.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by ANR within the framework of the PESTIPOND Project.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request due to restrictions. The data presented in this study are available on request and under conditions from the corresponding author (A.P.). The data are not publicly available because the data are part of the PESTIPOND project (financed by the French National Research Agency, ANR) which will be completed only in 2023.

Acknowledgments: The authors are very grateful to the staff of Laboratoire Ecologie Fonctionnelle et Environnement, for field samplings: B. Trochon and M.-J. Tavella, from the BIZ team and sample analysis: C. Pautot, W. Amblas, D. Lambrigot and F. Julien from the PAPC platform. E. Rabot and V. Dossantos are warmly thanked for GIS explanations. The authors would like also to thank the “Groupement des Agriculteurs de la Gascogne Toulousaine” (GAGT for farm surveys data). The Montoussé catchment at Auradé belongs to the French Research Infrastructure OZCAR (Observatory of the Critical Zone: <http://www.ozcar-ri.org/> accessed on 18 June 2021, © Copyright OZCAR 2020) and the Bassioué pond is also a VCG site of the LTSEZ Zone Atelier Pyrénées-Garonne (<https://pygar.omp.eu/> accessed on 18 June 2021, © Copyright 2021—Service de données OMP, SEDOO) which belongs also to the French Research Infrastructure RZA (Réseau des Zones Ateliers: <http://www.za-inee.org/> accessed on 18 June 2021, © Copyright CNRS 2015). OZCAR and RZA represent together the French contribution to the European Research Infrastructure eLTER.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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