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Damien A. Devault<sup>a</sup>; Chumnan Ith<sup>b</sup>; Georges Merlina<sup>b</sup>; Puy Lim<sup>b</sup>; Eric Pinelli<sup>b</sup>

<sup>a</sup> Cemagref Centre d'Antony, Parc de Tourvoie, 92163 Antony Cedex, France <sup>b</sup> École Nationale Supérieure Agronomique de Toulouse, Avenue de l'Agrobiopole, 31326 Castanet-Tolosan Cedex, France

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## Study of a vertical profile of pre-emergence herbicide contamination in Middle Garonne sediments

Damien A. Devault<sup>a\*</sup>, Chumnan Ith<sup>b</sup>, Georges Merlina<sup>b</sup>, Puy Lim<sup>b</sup> and Eric Pinelli<sup>b</sup>

<sup>a</sup>*Cemagref Centre d'Antony, Parc de Tourvoie, BP 44, 92163 Antony Cedex, France;*

<sup>b</sup>*École Nationale Supérieure Agronomique de Toulouse, Avenue de l'Agrobiopole, BP 32607  
Auzeville-Tolosane, 31326 Castanet-Tolosan Cedex, France*

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The fate of pre-emergence herbicides was investigated in sediment cores at sites selected for their nested sedimentation rates. Sediment was segregated in the coarse fraction ( $>63\mu\text{m}$ ) and in clays and silts ( $<63\mu\text{m}$ ) from the surface to a 45-cm depth. The fine fraction was more contaminated than the coarse fraction, mainly because of desethylatrazine (DEA). However, pesticides were observed in sediments at depths dated to before these compounds were used. Contaminated ancient sediments showed that contaminated elements migrated into the sediment. The fine fraction DEA profile was associated with the chronology of atrazine use. Comparing the sediment age, the half-life of the pesticides studied and banning dates showed that a non-degraded pesticide stock can be established in sediment.

**Keywords:** s-triazines; substituted ureas; anilides; pesticides; sediment; core

### 1. Introduction

Aquatic environments have been proven to be both rich and vulnerable, in part attributable to the sediment's integrative capacity. Modern contaminants occurring at critical levels in water bodies are pesticides and especially herbicides, the most widely used pesticides in the world and especially in Europe. Aquatic environments are most susceptible to contamination by pre-emergence herbicides. However, except for s-triazines, the fate of studied herbicides in the environment is poorly known because the analytical methods were developed too recently for these thermolabile compounds [1,2]. Their persistence could be enhanced by the sorption capacity of sediment for organic contaminants [3]. Coring allows chronological study of the deposit and the intensity of degradation using the ratio between chemicals and possible metabolites [4].

The persistence of 13 pre-emergence herbicides (s-triazines, substituted phenylureas and anilides) was studied. Even if the half-life of the herbicides studied is not documented in sediment, the literature reports their half-life in soil to be between a few days and six months [5]. Core sampling was performed at three Garonne River sites selected for their contrasting sedimentation rates. The vertical profile should provide information on *in situ* temporal persistence of pesticides in sediment and their fate on different and complementary time scales adapted to the unknown persistence of the pesticides: results

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\*Corresponding author. Email: damien.devault@cemagref.fr

from sediments with a high sedimentation rate ( $\leq 1$  cm/year) could give accurate information on these very labile pesticides' lifespan. On the other hand, results from sediments with a low sedimentation rate ( $\leq 0.1$  cm/year) provide a more historic picture. The aim of this study was to determine the persistence of herbicides in the environment and whether they persist long enough for chronological interpretation, as has been done for POPs [6–9], and hence their fate.

## 2. Experimental

### 2.1 Study site

Three Garonne River continuum sites (Figure 1) with common sedimentation regularity were sampled: (1) the Bourret wetland includes oxbow lakes due to meandering whose terminal mouth to the Garonne River is not closed where sedimentation results from floods ( $0.1 \text{ cm y}^{-1}$ ) where coring was performed; (2) the urban weir of Empalot (sedimentation:  $0.41 \text{ cm y}^{-1}$ ); and (3) the overflow Mancies dam (sedimentation:  $1.23 \text{ cm y}^{-1}$ ). Sedimentation proceeds in preserved lentic conditions on sheltered sites. The Bourret sampling site is located in a Garonne diverticule due to the downstream mouth of the closed Bourret oxbow, constituting a restricted area considering its flora and fauna. The Empalot sampling site is located in a cove included in the reservoir upstream from the eponymous urban weir present since 1183 AD. The reservoir was either cleaned out or broken since the 1900 flood. The Mancies dam was built in 1965 and the sampling

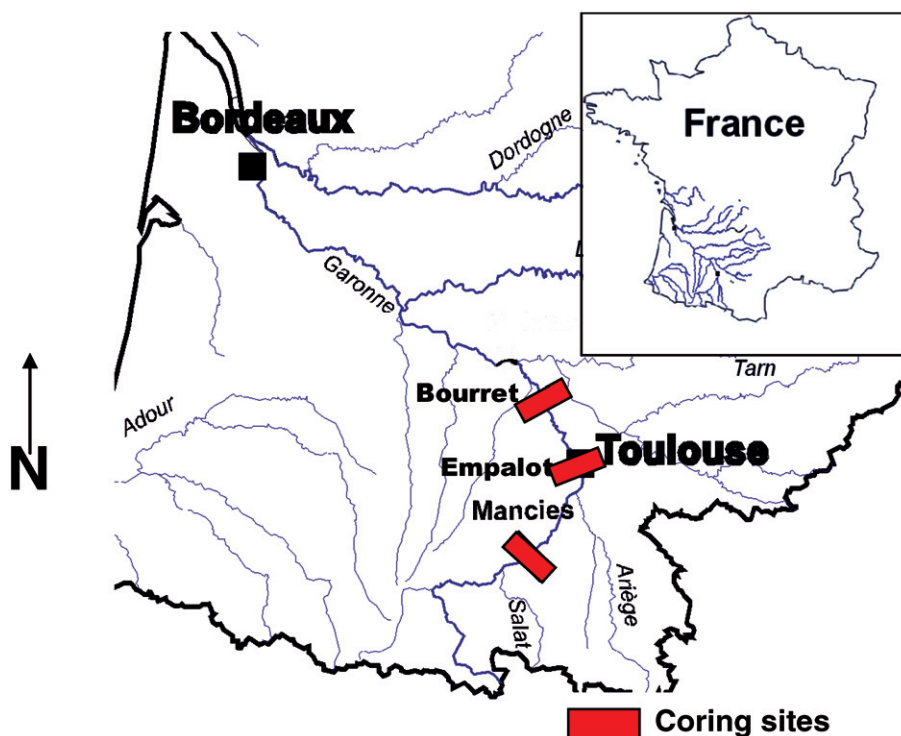


Figure 1. Coring sites map.

site was selected for its undisturbed property after previous studies from and thanks to the dam administrative. Sedimentation rates were obtained from data provided by the dam power supply owner, which were confirmed *in situ* by sonar and previous studies on the sedimentation rate in the Garonne River [10]. The sites were sampled using a 70-cm-long stainless steel core (diameter, 8 cm; volume, 3500 cm<sup>3</sup>). All the equipment was made of glass and stainless steel. Cores were divided into layers of varying thickness according to use and availability: 0–2, 2–6 and 6–14 cm to cover the surface sediment where early diagenesis occurs. Thirty- and 45-cm-deep layers were sampled when possible. It was impracticable except for Empalot at 45 cm. The samples were named by site (Mancies, CM1–CM5; Empalot, E1–E4; and Bourret, B1–B4) and depth, with the numbers corresponding to ascending order of the sampling depth (1, surface layer; 5, 45-cm-depth layer).

## 2.2 Analytical method

The sediment studied was air-dried and sieved through a 2-mm mesh. It was divided into a sandy fraction (>63 µm) and a fine fraction (<63 µm). The total organic carbon concentration was estimated with a Leco CS 125 (St. Joseph, MI, USA), the Renfield ratio with ThermoFinnigan CHNS C/N, and pesticides (DEA, atrazine, simazine, sebuthylazine, terbuthylazine, cyanazine, linuron, isoproturon, methabenzthiazuron, metolachlor, metazachlor) with a GC-MS HP5970 according to the method proposed by Devault *et al.* [2]. Briefly, extraction was performed with a Dionex Accelerated Solvent Extractor (ASE 200) (Dionex, Salt Lake City, UT, USA) using solvent mix (hexane/acetone, v/v, 1/1). Diatomaceous earth (Hydromatrix<sup>®</sup>) used for desiccation was from Varian (Palo Alto, CA, USA) and Florisil cartridges used for purification from Waters Corporation (Milford, MA, USA). Extracts were analysed in splitless mode (injector temperature, 280°C) set up at an initial temperature of 45°C. The first step had a temperature increase rate of 35°C min<sup>-1</sup> up to 180°C, then a second step at 8°C min<sup>-1</sup> up to 280°C and, finally, a 10-min plateau at 280°C. The detection conditions were temperature 300°C and E.M.V. 2600 V. All solvents were of analytical grade for pesticide analysis (Pestipur by SDS, Peypin, France). Pesticide standards (Mix 44), prepared by Dr. Ehrenstorfer GmbH (Augsburg, Germany), were purchased from CIL (Sainte-Foy-la-Grande, France) for quantifying the herbicides. The detection limits are presented in Table 2.

## 3. Results

The herbicide concentrations are presented in Table 1. DEA was found in the largest quantities, for all cores, with a greater than 2-mm average contamination of  $2.68 \pm 5.40 \mu\text{g g}^{-1}$ . This is the only pesticide present at all depths for all sites without E4 (fine fraction) and B2 (coarse fraction). Atrazine was also found frequently: 50% for whole samples, 57% in fine fraction, and 43% in the coarse fraction. The average atrazine contamination (considering whole <2-mm sieved sediment (Table 2) for all sites and depths) was  $0.18 \pm 0.23 \mu\text{g g}^{-1}$ . The other most pertinent pesticides were linuron ( $0.05 \pm 0.1 \mu\text{g g}^{-1}$ ) and metolachlor ( $0.04 \pm 0.06 \mu\text{g g}^{-1}$ ).

As for the pesticides stored in sediment less than 2 cm deep (Table 2), s-triazines accounted for 96.0% of the contamination. Anilides accounted for only 2.4% and

Table 1. Herbicide concentrations in fine and coarse fractions in sediment ( $\mu\text{g g}^{-1}$ ).

	DEA	Simazine	Atrazine	Terbutyl.	Sebutyl.	Cyanazine	$\Sigma$ . S-triazine	Isoproturon	Linuron	$\Sigma$ . Ureas sub.	Metolachlor	Metazachlor	$\Sigma$ . Anilides	Total
Fine fraction	CM1	0.07	—	—	—	—	0.33	—	—	—	—	—	—	0.33
	CM2	4.18	—	—	—	—	4.53	—	—	—	—	—	—	4.53
	CM3	0.43	—	—	—	—	1.24	—	—	—	—	—	—	1.24
	CM4	1.29	—	—	—	—	1.29	—	—	—	0.06	—	0.06	1.35
	CM5	0.02	—	—	—	—	0.03	0.02	—	0.02	0.04	—	0.04	0.10
	E1	0.77	—	—	—	—	0.77	—	—	—	—	—	—	0.77
	E2	5.44	—	—	—	0.06	5.80	—	—	—	0.07	0.10	0.16	5.97
	E3	0.33	0.05	—	0.17	0.02	0.74	—	—	—	—	0.02	0.02	0.76
	E4	—	0.06	0.04	—	—	0.30	—	0.21	0.21	0.06	—	0.06	0.58
	B1	22.37	—	—	—	—	22.37	—	—	—	—	—	—	22.37
Coarse fraction	B2	0.85	—	—	—	—	0.85	—	—	—	—	—	—	0.85
	B3	0.38	—	—	—	—	0.45	—	—	—	—	—	—	0.45
	B4	0.04	—	—	—	—	0.04	—	—	—	—	—	—	0.04
	B5	0.08	—	—	—	—	0.08	—	0.05	0.05	—	—	—	0.13
	CM1	T	—	—	0.01	—	0.03	—	0.01	0.01	—	—	—	0.04
	CM2	0.01	—	—	T	T	0.03	—	—	—	T	—	T	0.03
	CM3	0.01	—	—	—	—	0.01	—	T	T	T	—	T	0.02
	CM4	T	—	—	—	—	T	—	0.01	0.01	—	—	—	0.01
	CM5	0.01	T	T	0.00	—	0.01	—	T	T	—	—	—	0.01
	E1	0.01	—	—	0.03	—	0.04	—	—	—	0.12	0.09	0.21	0.25
	E2	0.05	—	0.01	—	—	0.19	—	—	—	—	—	—	0.19
	E3	0.05	—	0.02	—	0.03	0.09	—	0.22	0.22	0.07	T	0.07	0.37
	E4	0.02	—	0.01	—	—	0.05	—	—	—	0.06	—	0.06	0.11
	B1	T	—	—	—	—	T	—	—	—	—	—	—	T
	B2	—	—	—	—	—	—	—	—	—	—	—	—	—
	B3	0.02	—	—	—	T	0.02	—	0.04	0.04	—	—	—	0.05
	B4	0.03	—	—	—	—	0.03	—	0.04	0.04	—	—	—	0.07
	B5	0.11	—	—	—	—	0.11	—	—	—	0.12	—	0.12	0.23

— : less than detection threshold; T: herbicide traces ( $<0.01 \mu\text{g g}^{-1}$ ); Terbutyl.: terbutylazine; Sebutyl.: sebutylazine;  $\Sigma$ : total;  $\Sigma$  sub. phenylureas: total substituted phenylureas.

Table 2. Herbicide concentrations in >2 mm sediment ( $\mu\text{g g}^{-1}$ ).

	$\mu\text{g g}^{-1}$	DEA	Simazine	Atrazine	Terbutyl.	Sebutyl.	Cyanazine	$\Sigma$ s-Triazines	Isoproturon	Linuron	$\Sigma$ Sub. ureas	Metolachlor	Metazachlor	$\Sigma$ Anilides	Total	Age (year)
Stock	CM1	0.064	—	0.239	—	0.001	—	0.304	—	0.001	0.001	—	—	—	0.304	0–1.9
	CM2	3.998	—	0.335	—	T	T	4.333	—	—	—	T	—	T	4.333	1.9–5.6
	CM3	0.407	—	0.766	—	—	—	1.172	—	T	T	T	—	T	1.172	5.6–13
	CM4	1.263	—	—	—	—	—	1.263	—	T	T	0.059	—	0.059	1.322	30
	CM5	0.020	T	0.010	T	T	—	0.030	0.020	T	0.020	0.039	—	0.039	0.098	40
	E1	0.472	—	—	—	0.012	—	0.484	—	—	—	0.047	0.035	0.082	0.566	0–4.9
	E2	3.995	—	0.262	0.003	0	0.044	4.297	—	—	—	0.051	0.073	0.117	4.421	4.9–14.6
	E3	0.228	0.032	0.115	0.007	0.108	0.024	0.504	—	0.080	0.080	0.025	0.015	0.038	0.618	14.6–34
	E4	0.009	0.032	0.115	0.026	—	—	0.182	—	0.111	0.111	0.060	—	0.060	0.358	70
	B1	21.06	—	—	—	—	—	21.059	—	—	—	—	—	—	21.059	0–20
	B2	0.770	—	—	—	—	—	0.770	—	—	—	—	—	—	0.770	20–60
	B3	0.316	—	0.057	—	—	0.001	0.373	—	0.007	0.007	—	—	—	0.378	60–150
	B4	0.034	—	—	—	—	—	0.034	—	0.023	0.023	—	—	—	0.058	300
	B5	0.101	—	—	—	—	—	0.101	—	0.015	0.015	0.085	—	0.085	0.201	450
Detection threshold		0.005–0.001	0.001	0.005–0.001	0.001–0.0001	0.001	0.005–0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001		

— : less than detection threshold; T: herbicide traces ( $<0.01 \mu\text{g g}^{-1}$ ); Terbutyl.: terbutylazine; Sebutyl.: sebutylazine;  $\Sigma$ : total;  $\Sigma$  sub. ureas: total substituted phenylureas; Age: extrapolated age (year).

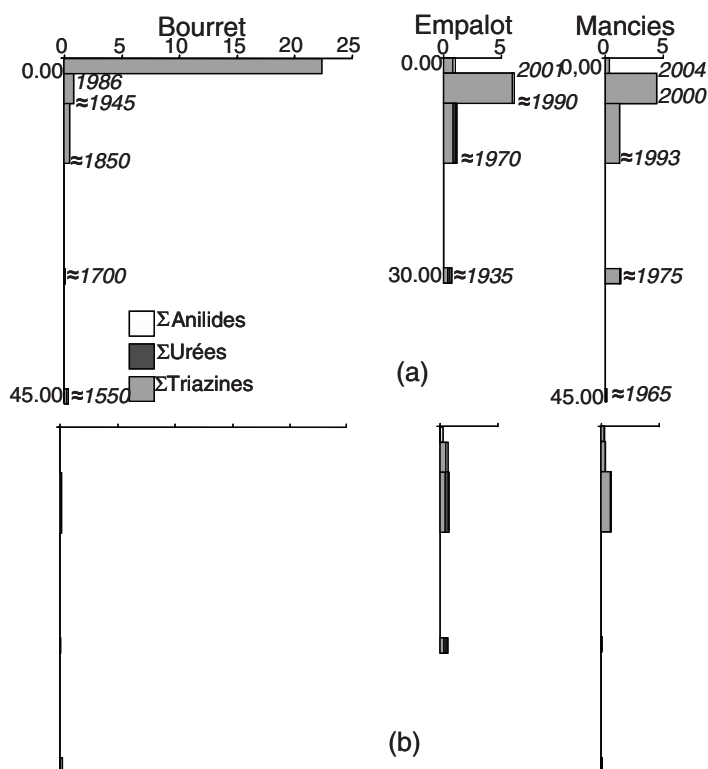


Figure 2. Less than 2 mm sediment concentrations: (a) DEA included (dates indicated in italics correspond to dates of the junction of layers); (b) DEA excluded.

Notes: Vertical axis: depth expressed in cm; Horizontal axis: concentration ( $\mu\text{g g}^{-1}$ ); Bourret sedimentation rate is about 1 mm/year, Empalot is about 4 mm/year and Mancies is 12 mm/year.

phenylureas 1.7%. DEA contamination totalled 88.7%. The conclusions for DEA take into account the B1 concentration but, without this value, DEA contamination still accounted for 56.6% of the total contamination. Consequently, conclusions on DEA remained unchanged even when rejecting the B1 value.

The most polluted site of the study was Bourret (average concentration of total herbicides in whole samples,  $2.71 \mu\text{g g}^{-1}$ ), mainly from DEA (98.6%) at the surface ( $22.37 \mu\text{g g}^{-1}$ ). Surface contamination accounted for 92.5% of the total contamination observed for this site due to the sedimentation rate law (see Section 1). The Empalot (mean stock,  $1.53 \mu\text{g g}^{-1}$ ) and Mancies sites (mean stock,  $1.68 \mu\text{g g}^{-1}$ ) showed similar contamination levels.

Sediment age was estimated layer by layer (Table 2) using the sedimentation rate. Herbicide amounts in sediments dated before 1946 accounted for 1.92% of the contamination observed (see Section 3.1). Reconstituted dates should be used with caution: reconstitution considers that sedimentation conditions have always been uniform. All the dates less than 15 years (before 1991) should be viewed with caution (Figure 2); nevertheless the calculated ages are given in Table 2.

Table 3 summarises the physical and chemical characteristics of the sediment samples studied. Sediment is dominated by silts. The C/N ratio indicated that the coarse fraction organic matter is mainly made up of plant remains.

Table 3. Physico-chemical characteristics of sampled sediment.

	Granulometry		TOC%		N%		C/N	
	inf 63	sup 63	inf 63	sup 63	inf 63	sup 63	inf 63	sup 63
CM1	91.18	8.82	2.65	6.57	0.32	0.42	8.20	15.63
CM2	95.63	4.37	3.36	6.68	0.31	0.40	10.84	16.52
CM3	94.45	5.55	4.28	8.35	0.36	0.46	11.98	18.12
CM4	97.92	2.08	3.45	14.00	0.29	0.75	11.71	18.68
CM5	97.95	2.05	2.60	3.97	0.24	0.26	10.95	15.07
E1	60.83	39.17	4.09	1.45	0.27	0.09	15.12	16.72
E2	73.20	26.80	2.83	1.41	0.28	0.10	10.20	14.11
E3	63.65	36.35	2.31	1.51	0.22	0.09	10.31	15.92
E4	52.83	47.17	1.82	1.25	0.19	0.09	9.76	13.83
B1	94.14	5.86	2.23		0.25		8.91	
B2	90.63	9.37	2.24	1.79	0.26	0.16	8.78	11.40
B3	82.12	17.88	0.66	1.71	0.14	0.13	4.78	12.83
B4	41.26	58.74	1.75	0.31	0.17		10.29	
B5	29.34	70.66	1.61	0.33	0.13		12.35	

#### 4. Discussion

The herbicide vertical profiles are not continuous. The detection limit may partly explain this because of the low contents detected close to the limit. Hence, it is difficult to interpret vertical profiles dominated by concentrations below the detection limit; consequently, the investigations will focus on the pesticides with higher detection rates.

##### 4.1 Chronologic interpretation

Given the quantity of atrazine and DEA in the sediment samples (Figure 2), the core chronological interpretation will be influenced by their profiles. These s-triazines, including atrazine, were used beginning in the 1960s and were heavily used in the 1980s and 1990s on the catchment area studied. s-Triazines and substituted phenylureas were banned in France in September 2003. By combining their sales (UIPP data, not shown) with each site's sedimentation rate, it appears that the fine fraction DEA profile is a tracer of contamination by s-triazines. Empalot and Mancies maxima were observed in layer 2 (between 2 and 6 cm deep) (Figure 2). However, the surface layer age (CM1 and E1) approximates the three year period since these pesticides were banned. The use of these s-triazines between 2003 and 2006 has been found in other studies [2] and is not inconsistent with an overall reduction in the use of these products from the time they were banned. In both cores investigated, contamination layers CM2, CM3, E2 and E3 can be interpreted as a decade-old residue of s-triazine pollution. For the core sampled in Bourret, most of the contamination was located in the surface layer (B1) (Figure 2). The core profile could be explained by the low sedimentation rate at Bourret: the surface layer accounts for approximately 20 years of contamination (Table 2). Prior use of herbicide compounds in France date from 1946. Herbicide concentrations found in sediment older than the invention of the pesticides studied must be interpreted as illustrating the vertical diffusion of herbicides within the matrix. The paradoxical contamination of deeper sediments is



probably attributable to re-emergence of contaminated groundwater, mainly ascendant or horizontal from aquifer to river [11]. However, this herbicide input, which remains minor compared to the particulate form from the runoff, is not sufficient to modify the conclusions considering the surface content.

#### 4.2 Atrazine and DEA

The metabolite DEA is predominant in the proportions presented above. This is not confirmed by other studies limited to surface sediment [2] even in lakes [12], invalidating the hypothesis of a run-off source of DEA. DEA was found mainly in the fine fraction, supporting the hypothesis of metabolisation mainly taking place in this fraction. Nevertheless, the vertical continuous profile of atrazine differs from the vertical continuous profile of its metabolite DEA. Moreover, the concentration of herbicides in the fine and coarse fractions was similar except for DEA, whose maximum fine fraction amounts were 100 times higher than the coarse fraction (see Table 1). Also, as DEA accounts for 88.7% of the stored pesticides measured, DEA magnitude can be considered to reflect the herbicides magnitude before degradation. The overall stored DEA is more than 15 times higher than the overall stock of atrazine. DEA has been the best tracer of atrazine pollution in the past. Also, DEA stored in the sediment provides indirect evidence of the relative use of atrazine during the corresponding periods. DEA concentrations are significantly higher than atrazine concentrations except in the surface layer. This proportion shows that, while the deterioration process has held constant for most pesticides, DEA is not easily degraded and remains adsorbed on the fine fraction despite its low  $K_{OW}$  ( $\log K_{OW} = 1.5$  [9]). Chefetz *et al.* [13] have shown that s-triazines can be divided into two categories: chlorinated and others. In a sorption-desorption study on sediment, they highlighted that the s-triazines carrying chlorine established links with a hydrogen bond carboxylic sediment, increasing their sorption and limiting desorption. These results underscore the affinity s-triazines have against substrates rich in COOH motifs, regardless of their  $K_{OW}$ . Desethylatrazine has a chlorine atom, which has similar properties that may explain why so much is present in the sediments. Therefore, even if DEA desorption depends on  $K_{OW}$  and another factor which could enhance the DEA persistence in the sediment, the same factors could enhance the persistence of other chemicals as well. It seems that the DEA content (indubitably higher than all the other pesticides studied) is more due to a deterioration lack, by less lysis or biodegradation.

#### 4.3 Degradation of herbicides

First of all, herbicide concentrations were quantified in layers that are too deep to be subjected to biodegradation, supporting the hypothesis of long-term persistence of herbicides in sediment.

Considering the observations that: (1) one core is from an urban site (Empalot); and (2) coring allows chronological study of the deposit as well as degradation intensity using the herbicide:metabolite ratio, the atrazine:DEA ratio was analysed. The DEA:atrazine ratio is representative of all cores. Insofar as the DEA is found in greater quantities in fine fraction where the vertical profile is complete, the fine fraction seems to be the fraction where transformation occurs, as described elsewhere [2]. The average DEA:atrazine ratio weighted by the granulometric importance of each layer was established for both fractions

in each core. The coarse fraction DEA : atrazine ratio of each core was used to balance the spatial variability between the sampling sites (some sites are more contaminated than others). The fine fraction ratios were divided by the ratios of the corresponding coarse fraction. The ratio obtained for Empalot was 12.25, 3.92 for the central part of the retainer Mancies (CM) and 3.52 for Bourret. Unquantifiable traces (T) were estimated at half of the detection limit –  $0.005 \mu\text{g g}^{-1}$  – and undetectable concentrations were estimated at  $0.002 \mu\text{g g}^{-1}$  (see Table 2). Similarly, pesticides from less persistent families (substituted phenylureas and anilides) also showed relatively large quantities in the Empalot core.

Degradation activity at Empalot seems low compared to other sites whose values were very similar, which may result from the urban context and various pollutants associated with high densities of human waste (pharmaceuticals, antibiotics, persistent organic pollutants, polycyclic aromatic hydrocarbons, metals, etc.). This mixture of pollutants affecting life conditions may hinder bacterial activity. Considering this potential misunderstanding, the denitrification intensity was followed up for the three sites because the denitrification process dominated in the bacterial communities in the Garonne River sediment [11]. Denitrification intensity results did not present significant difference between the three sites so, the results of this experiment did not argue in favour of urban bacterial activity limitation hypothesis. In the absence of a recent, unobserved, massive urban or suburban polluted deposit, improbable in this permanently monitored urban site. Given the state of affairs, it seems premature to conclude. Nevertheless, even if a denitrification difference had not been observed, studies conducted nearby in the Middle-Garonne flux [15] provide substantial indications on the complexity of the *in situ* degradation process and confirm that complementary studies are necessary to draw firm conclusions.

## 5. Conclusion

This experiment provides valuable new information:

- (1) The fine fraction is more contaminated than the coarse fraction. DEA is mainly distributed in the fine fraction.
- (2) Herbicides are found in deep abiotic layers, with aging or other processes increasing pesticides' half-life possibly involved. The presence of pesticides in ancient sediments shows that ancient sediments (>15 cm deep) may be contaminated by pesticides that did not exist at the time the sediments were formed, indicating that contaminated elements may arise from migrations from the surface layer or the water table.
- (3) Only the DEA profile in the fine fraction seems to show chronological interpretative properties. The disproportion between DEA levels and the levels of parent pesticides shows that sediments were contaminated before metabolism, mainly in the fine fraction.

Comparing sediment age, the half-lives of the pesticides studied and of the dates these substances were banned shows that the establishment of a stock of non-degraded pesticides is possible in sediment. *In situ* remanence of pesticides [14] is thus substantially increased compared to *in vitro* experiments, confirming Eganhouse *et al.* [15], who indicated a 100- to 1000-fold lower degradation speed in sediment cores.

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