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Herbicide accumulation and evolution in reservoir sediments

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A B S T R A C T

The aim of the present study was to understand the effect of reservoir configurations on sediment pesticide fate. Two dams were selected on the River Garonne, in southwest France: Carbonne and Golfech, both with reservoirs subject to accumulation of herbicide-contaminated sediment. They are situated upstream and downstream respectively of an agricultural and urban area: the Mid-Garonne. The results presented include pesticide concentrations and C/N ratios in the smaller sediment particles (<2 mm) and values of oxygenation and herbicide concentrations in the water.

The dynamic behaviour of sediment in the reservoirs is discussed. The present study shows that the theoretical lifespan (weak remanence *in vitro*) and the results actually observed in the sediment are conflicting. Pesticide contamination in Carbonne indicates conservation, even accumulation, of herbicide molecules while in Golfech transformation processes clearly dominate. The hydromorphological position of Golfech reservoir, i.e. located at the junction of two rivers with contrasting hydrological regimes and very different oxygenation conditions, leads to accelerated pesticide desorption or degradation. Unfortunately, this configuration is rare.

Keywords:
S-triazines
Substituted ureas
Anilides
POPs
Water
Sediment
Dams

1. Introduction

The 40,000 dams in the world present various proven disadvantages (Giles, 2006). Sediment, especially coming from upstream, can be the vector of pollutants, including herbicides (Devault et al., 2007), affecting the food networks (Frery et al., 2001). The pollutants accumulate in the dam essentially after having arrived from upstream via the river (Doggett and Rhodes, 1991) and pesticide accumulation in sediment causes strong contamination especially of the benthos (Armstrong et al., 1980). Hormonal and behavioural disruption due to pesticides can prove (Scott and Sloman, 2004) to be lethal at the top of the food net (Heger et al., 1995). Although herbicides such as s-triazines, substituted ureas and anilides account for 47% of the world pesticide trade, they have been the object of a few environmental studies (Gao et al., 1997, 1998) due, in particular, to methodological problems especially for substituted ureas and anilides. Those two families of pollutants are more labile *in vitro* than the abundantly-documented persistent organic pollutants (POPs) or, to a lesser extent, s-triazines. So, they are considered to be short-lived and milder even though very few conservation data exist.

The aim of the present study was (i) to gain a fuller understanding of the phenomena affecting herbicide remanence in sediment, (ii) to investigate the effect on pesticide fate of two hydromorphologically and physico–chemically contrasting large reservoirs on the same river continuum and (iii) to determine which dam layout will minimize pesticide impact on the environment.

2. Study area

France is the second agricultural producer state in the world and the first in Europe (UIPP, 2008). France is the fourth pesticide consumer state in the world and the first in Europe (UIPP, 2008). The Mid-Garonne has been largely described elsewhere (Devault et al., 2007) for human settlement, pedo-morphologic, hydrologic and use characteristics. The Garonne River is the third largest river in France (Fig. 1) and structures the Mid-Garonne, an area included between two dams on the Garonne River: Carbonne and Golfech. The fifth largest city in France, Toulouse with a population of 1 million is located in the Mid-Garonne.

Carbonne dam (Fig. 2) is the last of the hydroelectric installations of the Pyrenean Piedmont. It forms the upstream limit of the Mid-Garonne,

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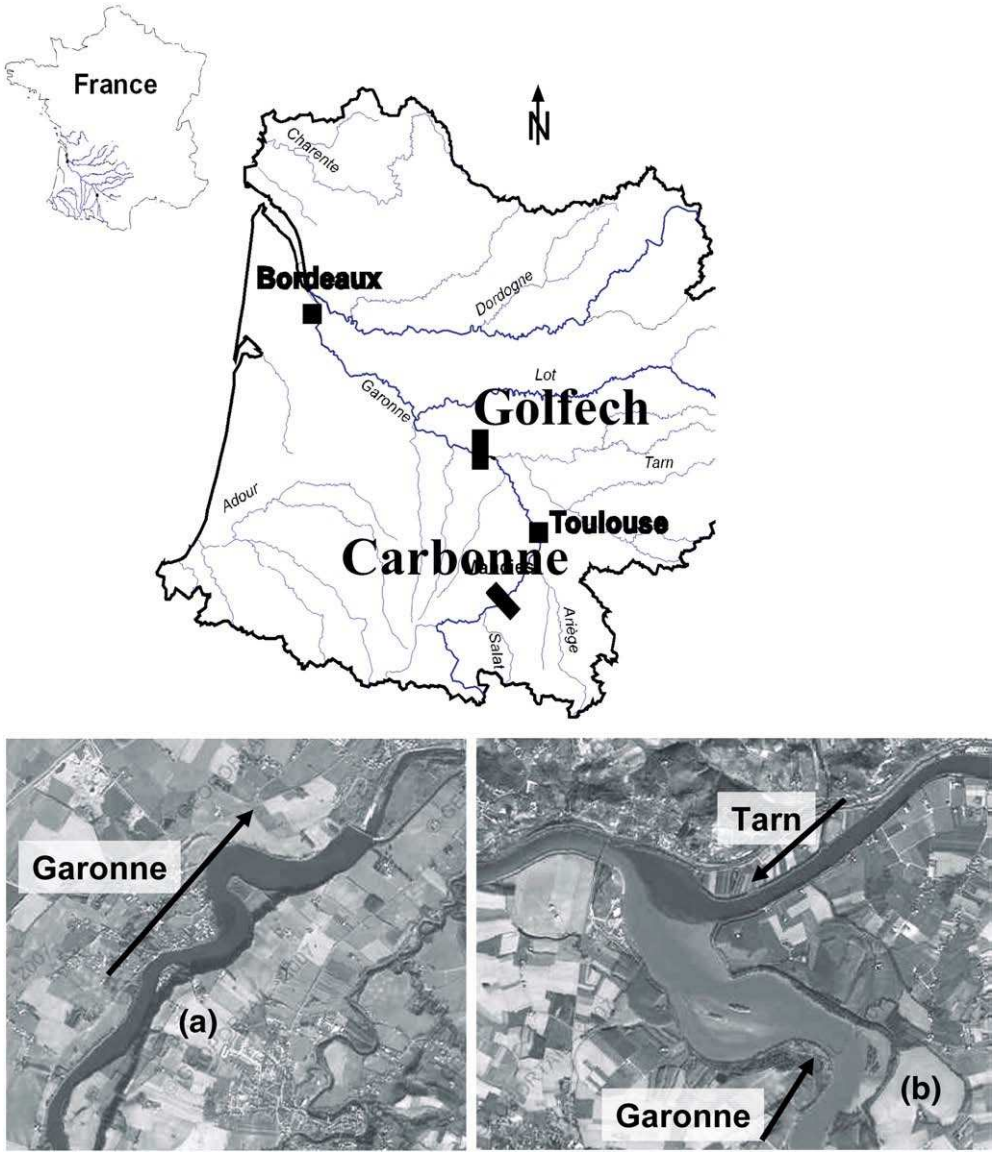


Fig. 1. Location of the sampling sites and aerial (Géoportail, 2007) views of Golfech reservoir (a) and Carbonne reservoir (b).

a simple dam across the river with no other particular features: the vast majority of dams in France have the same configuration. Upstream of Carbonne, the Pyrenean Piedmont is primarily used for livestock while field crops start to become preponderant near the reservoir (8,000,000 m^3), located in the transition zone. The second dam in this study, built for the production of hydro-electricity in 1968, is at Golfech (Fig. 3). It is located at the junction of the Garonne with its largest affluent: the Tarn River and forms the Golfech reservoir (25,000,000 m^3), which is the downstream limit of Mid-Garonne. Locating a dam on a confluence is very unusual, occurring only once in the whole of the 296 dams in the basin. The configuration of the dams is their only structural difference: Golfech and Carbonne are both constant-head dams, accommodate fishing and sailing, have the same length (3.5 km) and water residence time. Their reservoirs are both protected as zones of high ecological richness and for this reason, they are never drained. The present study seeks to understand the processes which condition the fate of pesticides in the sediments of the reservoirs, each with its own configuration.

Large quantities of pesticides are applied on the slopes in the Mid-Garonne, subjected to significant levels of erosion. The main type of pesticide to be spread is herbicide and its uses are urban as well as agricultural. Unfortunately, no data of local pesticide consumption or use is available to estimate the quantities entering the river. However, even if such data were available, interpretation would be subject to caution because of the slow release of compounds into surface water from contaminated groundwater and soils.

3. Materials and methods

Water was taken at the surface and kept at 4 °C in darkness until analysis. Raw water was analysed for both reservoirs. Filtered water was analysed only for Golfech reservoir.

The sediment was taken with an Eckmann bucket at the sites indicated in Figs. 2 and 3. At Carbonne reservoir, six samples were taken while at Golfech, to respect the ratio of reservoir areas, eleven were studied. Sampling sites were chosen in Carbonne and especially Golfech to follow the main Garonne riverbed. Sampling and analysis were performed using a method validated in Devault et al., 2007 which reports the justification for the choice of herbicide families studied, the high significance of large samples (400 cm^2, 1 kg of homogenised

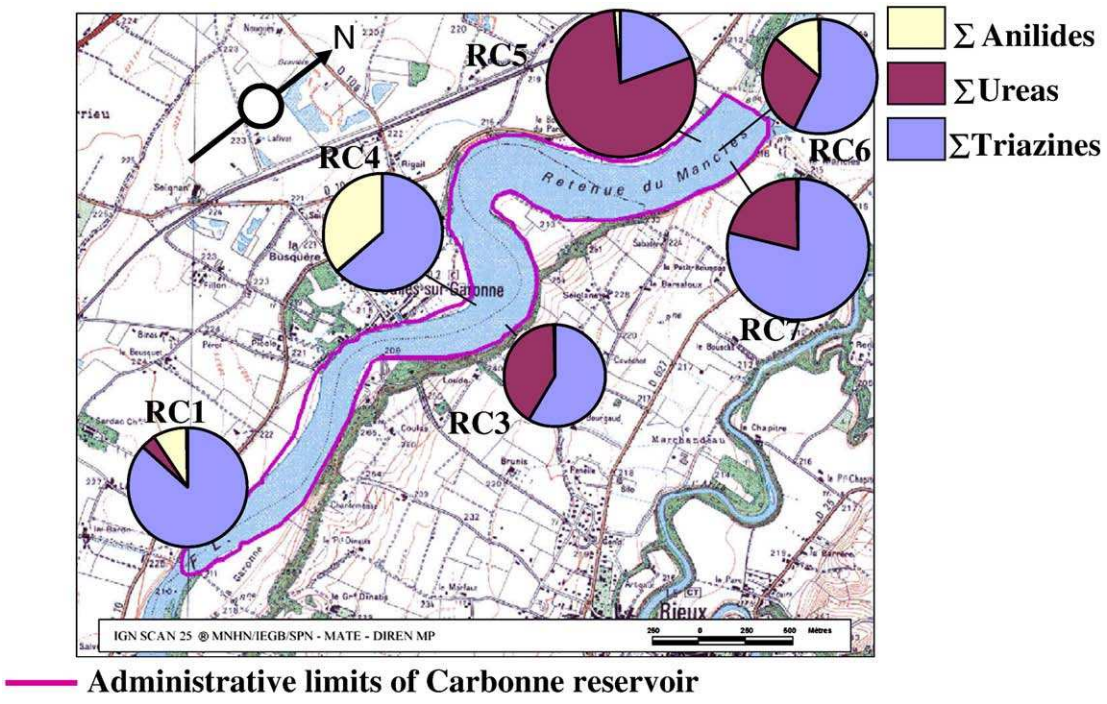
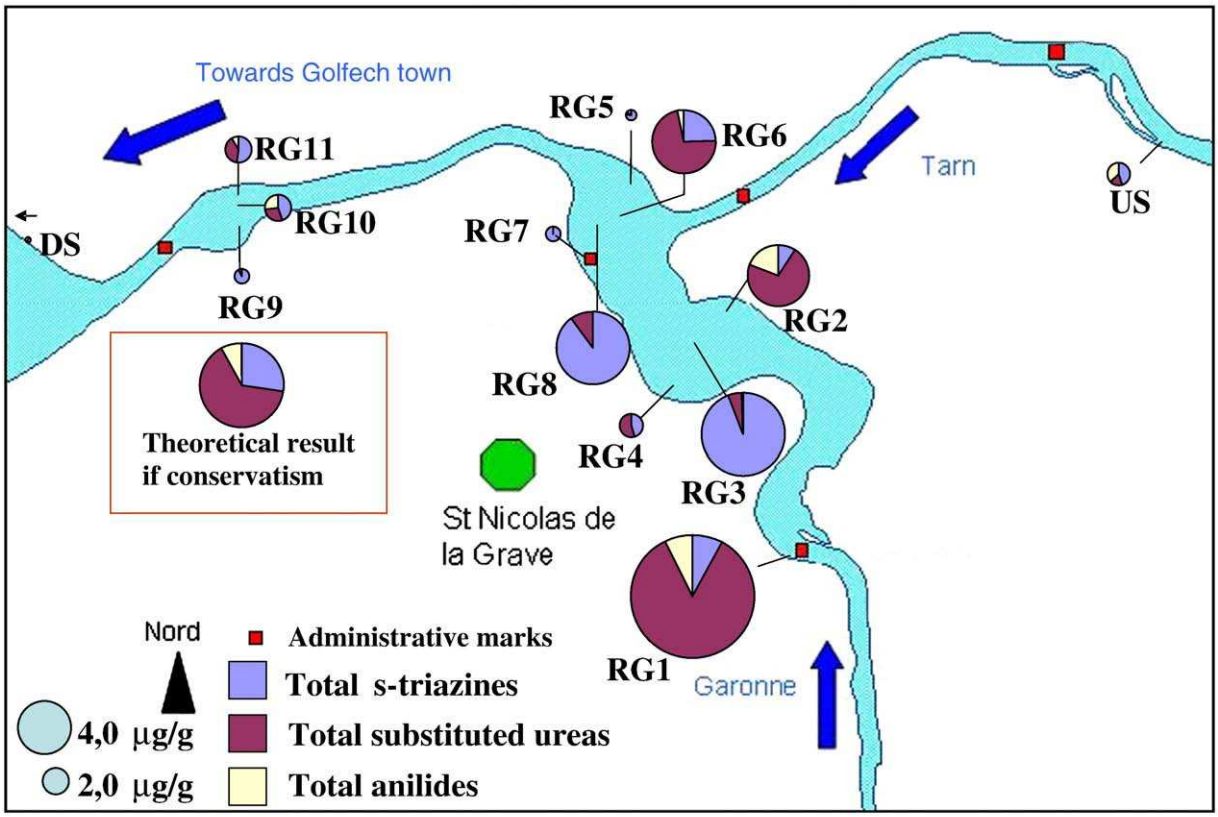


Fig. 2. Geographic distribution of herbicide contamination in Carbonne reservoir.

sediment samples) and the high performance of the analytical method (high accuracy with 1 ng/g-detection limit and high reproducibility). Triplicates were performed but, as for Devault et al. (2007), repeatability was indiscernible to the instrumental background noise.

3.1. Sampling period

The sediment samples were taken simultaneously on March 16, 2005, at the lowest winter water level. The monthly spreading



Pesticides – Sediment sampling –March 2005

Fig. 3. Geographic distribution of herbicide contamination in Golfech reservoir.

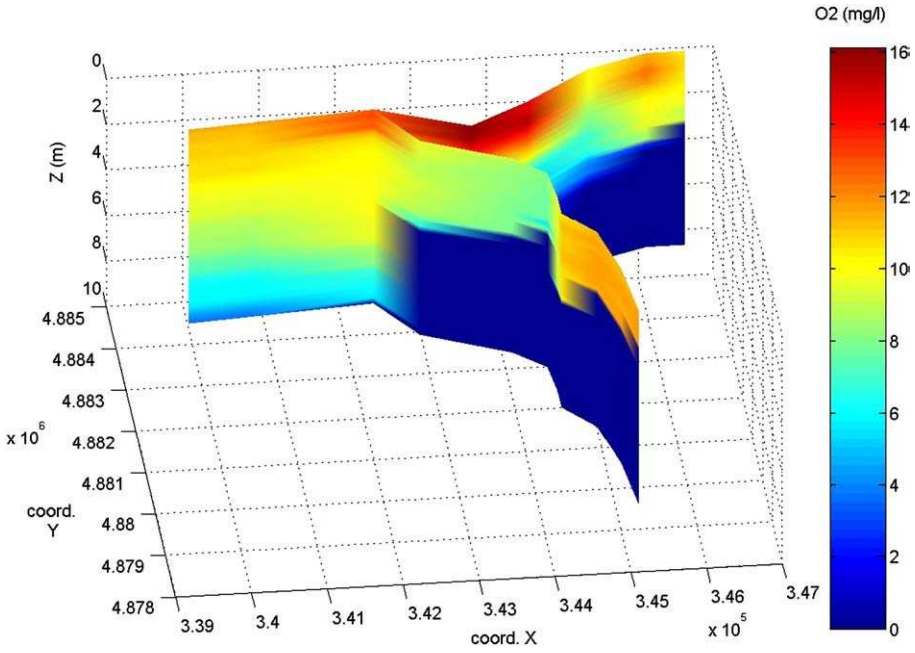


Fig. 4. Water oxygen (mg/L) in Golfech reservoir. *X*, *Y* and *Z* are the spatial coordinates of the reservoir (*Z* is the depth).

intensity of pesticide use in March corresponds to the annual average intensity of pesticides spreading. The temperature remained at typical winter values (around 5 °C).

3.2. Sampling treatment

3.2.1. Water

Extraction was performed on samples where the pH had been adjusted to 7, filtered through GFF membrane. Solid-Phase Extraction (Supelclean vacuum device) of 200 ml samples was performed with silica cartridges grafted with Supelco C18.

Analysis of raw water is detailed in Devault et al., 2007. The three-dimensional profile of the water oxygen content was measured on site with an oxygen electrode. The Golfech profile includes results obtained on the Garonne branch of the reservoir, the Tarn branch and at a point between the confluence and the dam (Fig. 4).

3.2.2. Sediment

Herbicide content was analysed as explained elsewhere (Devault et al., 2007). Briefly, fine (lower than 63 µm-mesh) and coarse (between 63 µm and 2 mm-mesh) fractions of dry sample were extracted by ASE 200 then purified on Florisil cartridges and quantified with an HP5290 GC-MS. Whole sediment, i.e. all particles smaller than 2 mm, was reconstituted by calculation. Herbicides from the standard Mix44 provided by Cluzeau Info Labo (Sainte-Foy-la-Grande, France) and produced by Dr Ehrenstorfer Gmbh were also quantified.

Carbon was measured with a CS-500 Determinator (Eltra GmbH, Neuss, Germany) and nitrogen by the Kjeldahl method. For the needs

Table 1
Herbicide concentration (µg/g) of sediment finer than 2 mm

	RC1	RC3	RC4	RC5	RC6	RC7	US	RG1	RG2	RG3	RG4	RG5	RG6	RG7	RG8	RG9	RG10	RG11	DS
>63 µm (%)	0.02	0.05	0.3	16.77	0.02	0.01		0.02	0.52	0.27	0.01	0.52	0.06		0.3	0.87		0.19	1.40
<63 µm (%)	33.65	0.89	0.89	23.16	0.89	0.89	32.04	26.8	26.96	88.04	98.97	2.73	4.1	3.6	3.87	15.78	15.92	15.89	58.30
<2 mm (%)	66.33	99.06	98.81	60.07	99.09	99.1	67.96	73.18	72.52	11.69	1.02	96.76	95.84	96.4	95.83	83.35	84.08	83.92	40.30
C/N>63 µm	12.60	9.72	10.66	11.19	10.52	11.31	6.64	11.43	8.88	7.74	4.62	11.82	7.14	5.99	7.60	10.55	7.69	11.76	9.09
C/N<63 µm	6.38	7.29	6.45	7.53	7.10	7.31	4.74	5.44	5.99	4.34	5.50	7.97	4.16	5.23	5.59	6.35	5.17	5.12	6.90
C/N<2 mm	8.47	7.3	6.47	7.12	7.12	7.34	5.35	6.99	6.74	7.32	4.63	8.04	4.28	5.25	5.648	6.957	5.573	6.164	8.08
DEA	0.35	0.69	0.87	0.11	0.13	0.29	0.20	0.54	0.32	0.11	0.16	0.17	0.43	0.33			0.18	0.47	
Simazine		0.15	0.00	0.13	0.40	0.27	0.53					0.12	0.13	0.25	0.64	0.27	0.14	0.33	0.05
Atrazine	0.37		0.19	0.24	0.26	0.85	T								0.50	0.21			
Terbuthylazine	0.36				0.24			0.10	0.12	0.10	0.31		0.14	0.45			0.31		
Sebuthylazine							0.05			5.26	0.21	0.08	0.22	0.38					
Cyanazine	0.95	0.34	0.44	0.10	0.26	0.78	0.01	0.10	0.16	0.41	0.14	0.24	0.24	3.62		0.53	0.27	0.26	0.20
Hexazinone																			
Total triazines	2.03	1.18	1.50	0.57	1.29	2.19	0.79	0.74	0.60	5.88	0.81	0.61	1.18	5.02	1.14	1.01	0.90	1.06	0.24
Metabenz.	T						0.01						0.30				T		
Metobromuron				1.56				0.55	0.36	0.05	0.70		1.20	0.12		0.77	0.32	0.08	
Isoproturon							0.20	3.73	4.06		0.26				T				
Linuron	0.10	0.83		0.74	0.67	0.59	0.11	3.63	0.32	0.28	T	0.06	1.96	0.43	T	T	0.25		
Total ureas	0.10	0.83	0.00	2.30	0.67	0.59	0.32	7.92	4.74	0.33	0.97	0.06	3.46	0.55	T	0.77	0.56	0.08	
Metolachlor	0.21			0.04	0.14	T	0.01	0.11	0.67	0.03	T	0.11	0.14			0.16	0.54		
Metazachlor			0.86		0.17		0.63	0.57	0.59		T	T							0.15
Total anilides	0.21		0.86	0.04	0.31	T	0.65	0.67	1.26	0.03	T	0.12	0.14			0.16	0.54		0.15
Total	2.34	2.01	2.36	2.91	2.27	2.78	1.75	9.33	6.60	6.24	1.78	0.79	4.78	5.57	1.15	1.95	2.01	1.15	0.40

RC1 to RC7 correspond to samples from Carbonne; RG1 to RG11 from Golfech. US: Tarn upstream of Golfech. DS: Garonne downstream of Golfech.
T: concentration lower than 0.01 µg/g. No value: undetectable concentration/percentage equal to 0. Metabenz: metabenzthiazuron.

of this particular study, only the C/N ratio was useful to qualify the organic matter (a high C/N ratio distinguishing Cormophytes remaining alive or undergoing humification while a low C/N corresponds to everything else from the biota).

4. Results

4.1. Water

Neither raw nor filtered water presented any detectable herbicide concentrations at either Golfech or Carbonne.

4.2. Sediment

4.2.1. Physical–chemical parameters

The C/N ratios in the fine fraction were fairly low (typical of proteins) while in the course fractions they were relatively high (representative of highly humified plant matter).

Fig. 4 shows the dissolved oxygen profile in Golfech reservoir. Dissolved oxygen values were between 2 and 16 mg/L. The Tarn branch showed the highest levels with saturation of surface water while the Garonne branch presented particularly low values for surface water especially when compared to the high Tarn branch values.

4.2.2. Herbicides

The study found measurable herbicide concentrations in all sediments of particle size lower than 2 mm but in fact in the study was carried out on two separate fractions i.e. smaller than and larger than 63 µm. The coarser fraction (>63 µm) provided information on the contamination of organic matter undergoing humification (Table 1).

Expressed in µg of the herbicides per gram dry weight of sediment, the average herbicide concentration, pooling both reservoirs, was 3.24± 2.31 µg/g. In Carbonne, it was 2.44±0.33 µg/g, and 3.64±2.77 µg/g in Golfech.

S-triazines prevailed: 1.59±1.48 µg/g on average for both reservoirs representing 49% of total contamination, accounting for 45.4% (1.65±1.79 µg/g) in Golfech and 60% (1.46±0.59 µg/g) in Carbonne. Substituted ureas, with an average concentration for the two reservoirs of 1.37±2.07 µg/g, accounted for 42.3% of the total contamination by herbicides i.e. 46.2% (1.68±2.45 µg/g) in Golfech and 30% (0.75±0.83 µg/g) in Carbonne. Anilides represented, overall, only 8.7% of the herbicides found (0.28±0.37 µg/g) i.e. 10% (0.24±0.33) in Carbonne and 8.4% (0.31±0.41 µg/g) in Golfech. Owing to the relatively high standard errors, the differences between the two reservoirs for each family of herbicides were not significant.

Of the six sampling sites on Carbonne reservoir, the least contaminated was RC3 with 2.01 µg/g and the most was RC5, primarily containing substituted ureas (79% of total contamination): due to metobromuron which peaked at 1.56 µg/g. Ureas were undetectable at RC4 where, on the contrary, anilides peaked

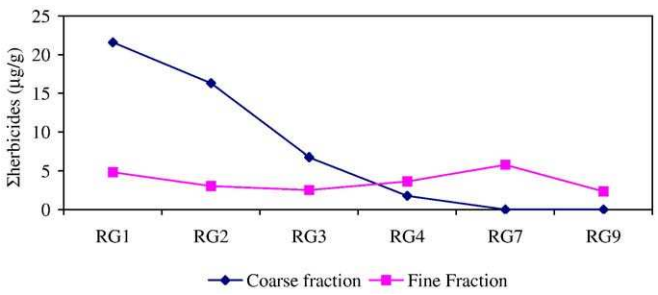


Fig. 5. Evolution of herbicide concentration depending on granulometric fractions in the Garonne Channel of Golfech reservoir.

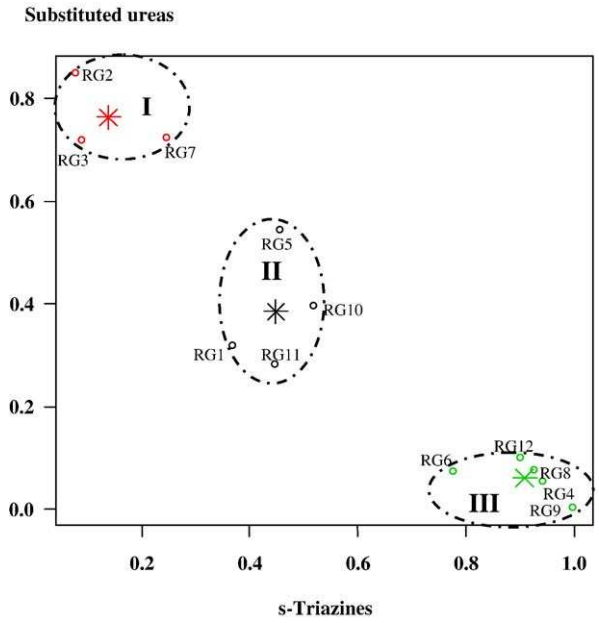


Fig. 6. Unsupervised classification of sampling sites in Golfech depending on their herbicide contamination. Top left (group I): RG2, RG3 and RG7. Centre (group II): RG1, RG5, RG10 and RG11. Bottom left (group III): RG4, RG6, RG8, RG9 and RG12.

(0.86 µg/g metazachlor). Anilides were undetectable in RC3 and RC7 where s-triazines (mainly atrazine) were maximal (2.19 µg/g). Of the twelve sampling sites on Golfech, the least contaminated was RG5 (0.79 µg/g) while the most contaminated was RG1 with 9.33 µg/g herbicides, primarily with substituted ureas (7.92 µg/g). S-triazines reached a maximum in RG3 (5.88 µg/g) and a minimum in RG2 (0.60 µg/g) where, anilides reached a maximum. Anilides were undetectable in sampling sites RG4, RG7, RG8 and RG11.

The sampling sites in Golfech reservoir allowed the contamination profile to be determined in the different particle size fractions (Fig. 5). Although the contamination of the fine fraction varied insignificantly , the herbicide contamination of the coarse fraction (very high at the transition between lotic and lentic water marking the entrance to the reservoir) decreased in the reservoir until it was no longer detectable. Unfortunately, no profile was measured for the Tarn channel due to its shorter length in Golfech reservoir. In Carbonne reservoir this trend was not observed, contamination remaining constant across the particle size fractions.

4.2.3. Statistics

Statistical analyses were performed using the free software R. Firstly, we compared the variance of the contaminant concentrations in Golfech reservoir to their variance in Carbonne reservoir. Secondly, we investigated the spatial distribution of the contaminants just in Golfech reservoir.

Firstly, F-tests were conducted to highlight any differences in herbicide concentration variance between the two reservoirs. For all 17 sampling sites overall herbicide concentrations were computed as the sums of s-triazine, substituted urea, and anilide concentrations. Herbicide concentrations in both reservoirs were both normally distributed as indicated by Shapiro-Wilk tests ($p=0.54$ and $p=0.06$ respectively). An F-test indicated that the variances of the herbicide concentration were significantly different ($p=0.0002$) in the two reservoirs. The standard deviation of the herbicide concentration was lower in Carbonne (0.33 µg/g) than in Golfech (2.77 µg/g), Golfech therefore having the more heterogeneous distribution.

In the second step, we investigated the spatial distribution of the contaminants in Golfech reservoir. In the following we consider the proportions of a contaminant in the whole <2 mm sediment fraction.

By using proportions (the sum of the 3 herbicide families are equal to 1 at each sampling site), we can consider two herbicide families only. Anilide contamination represented just 8% of the overall contamination within Golfech reservoir, so only the variations of s-triazine and substituted urea are followed below. In Fig. 6, the x and y axes correspond to the proportions of s-triazines and substituted ureas respectively. The 11 sampling sites were classified using the k-means method of hierarchical decomposition in three groups. The first group (group I, RG1, RG2, RG6) presents a prevalent of cumulated concentration of substituted ureas (barycentre I coordinates: $x=0.14$, $y=0.76$). The second group (group II, RG3, RG5, RG7, RG8, RG11) is in an intermediate position (barycentre II coordinates: $x=0.45$, $y=0.38$). The third group (group III, RG3, RG8, RG9) shows the prevalence of s-triazines (barycentre III coordinates: $x=0.91$, $y=0.06$). The 2D data were then projected into an 1D composite data set using linear discrimination analysis. Each projected group was distributed normally (Shapiro, pI = 0.88, pII = 0.59, pIII = 0.99). Welch tests significantly refuted any similarity between groups (pI,II = 0.004, pI,III = 0.0003, pII, III = 0.000015). These results show that herbicide proportions in the Golfech reservoir can be significantly classified into groups pI, pII and pIII. The first group gathers sampling sites close to the entrance to the reservoir, the second group consists of internal sites, and the third group is composed of sampling sites close to the end of the reservoir.

5. Discussion

As underlined elsewhere (Devault et al., 2007), the reservoir sediments were more polluted than the river from which they came (3.50 ± 1.58 μg/g for reservoirs versus 0.65 ± 0.65 for riverwater). It is regrettable that *in situ* herbicide contamination has not become the object of more studies (Gao et al., 1997, 1998) or analyses on this scale of events. Studies of lakes do exist for POPs, such as those of Rawn et al. (2001), Marvin et al. (2004), Peris et al. (2005). The remanence of these contaminants also allows degradation studies on sediment cores (Stern et al., 2005). The present study does not focus on the origin of the pesticides i.e. due to urban or agricultural activities. We will firstly focus on demonstrating the elimination potential of each type of dam, secondly the resulting herbicide remanence and thirdly on the nature of this elimination potential.

The standard deviations of herbicide concentrations in Carbonne reservoir (0.33 μg/g) indicate that herbicide contamination is more homogeneous there than in Golfech reservoir (2.77 μg/g). In fact herbicide concentrations measured at Carbonne reservoir sampling points did not vary significantly. On the contrary, the sediment at the exit of Golfech reservoir was found to contain significantly less pesticide than at the entrance. The mean herbicide concentration of sediment at the Golfech input was 6.11 μg/g. The herbicide concentration at the head of the reservoir (RG9, RG10 and RG11) was 1.70 ± 0.48 μg/g. Thus, considering that in Golfech reservoir, 60% of the water flow comes from the Garonne and 40% from the Tarn, the concentration at the entrance (Fig. 6 group I, RG1, RG2 and RG6 —even though RG6 is located in a mixing zone, indicating that contamination is reduced) was 3.59 times higher than that at the head of the reservoir, indicating loss or transformation of the herbicides within the reservoir. This upstream/downstream ratio increases to 15.3 times if the total herbicide concentration of the sediment at the entrance to Golfech is compared to the concentration in the sediment sampled downstream of the reservoir (DS). This indicates greater conservation of the parent herbicides in Carbonne reservoir, where no significant variation was noted, than in Golfech. Similar calculations comparing various sites near the inputs (US) or the outlet (RG9, 10, 11, DS) corroborated lower concentrations downstream than upstream in Golfech both for the fine fraction and the coarse fraction, although in the coarse fraction loss or transformation of the parent herbicides occurred faster than in the fines. The irreversible binding hypothesis should be rejected because of the similarities in the bottom sediment from Carbonne and from Golfech, excluding the possibility that irreversible binding occurs in Golfech (making the herbicides non-extractable) and not in Carbonne. This concentration reduction observed for both particle classes, excludes any artefacts that could be due to different rates of sediment transport for different particle sizes. In addition, the above calculations assume that pesticide input to reservoirs is constant. However, (i) most of the herbicides studied have been prohibited fairly recently, or at least subjected to limitations of use (ii) the results presented were thus obtained in a general context of reduction in the consumption of the active molecules considered. Since 1999, the combined tonnage sold in France has decreased by 40.5% according to UIPP, 2008. Similar data (not shown) concerning organochlorines give further weight to our conclusions. Thus, whereas conservative transport dominates in Carbonne reservoir, transformation seems to be the major process in Golfech.

In future investigations, the temporal scale of sediment transport within reservoirs should be estimated. Knowing how long it takes for sediment to cross a reservoir is of primary importance when the aim is to determine the reality of the remanence of the active molecules occurring in practice. According to the literature, the herbicide molecules analysed here have a half-life in the soil of five days to five months (BCPC, 2006).

As stated, Golfech and Carbonne reservoirs occupy equal lengths (3.5 km). The mean velocity of the water can be estimated as equal between Carbonne and Golfech reservoirs by calculating the residence time. However, hydrodynamic complexity prevents any estimations of sediment residence time from being calculated but analogy is possible with the largest French river, the Loire. The sediment transport velocity in the Loire has been estimated at 10 m/day for a section without obstacles (Belleudy, 2000, 2001) in a sector which shares the same slope and morphopedology (hills with leached and/or degradated soils) as the Garonne in the present study. Progressing at this pace, the sediment entering the 3.5 km-long reservoirs of Golfech or Carbonne would take approximately one year (around 350 days) to cross the dam. The process should be the same for both reservoirs. The estimate of an absolute minimum residence time of one year can be regarded as the high estimate; i.e. with maximal mean velocity. Thus, the residence duration of sediment in the reservoirs is at least one year. So, depending on the time scale involved, metabolisation should be observed. The literature values (BCPC, 2006) suggest that degradation of the pesticides within reservoirs should be complete. The present field results indicate that the herbicides persist much longer, in a way never envisaged in theoretical frameworks designed from data obtained with *in vitro* experiments designed according to the short *in vitro* lifespan. However, transformation was faster in Golfech (still involving at least a one-year process) compared to Carbonne (without any decrease in herbicide content).

The potential for herbicide elimination could be due to different concomitant factors. The Carbonne dam, typical in its configuration, is built perpendicularly to the flow of the river with neither a confluence nor any another disturbing hydrological feature. The use of large river confluences to place a dam is indeed exceptional, Golfech being the only one of 296 in the whole Garonne basin (AEAG, personal communication). After statistical analysis, the differences in horizontal spatial distribution of herbicides in >2 mm sediment were mainly attributed to this topographic difference. The elimination potential could be determined by transformation or enhanced desorption. Transformation can be of two types: simple lysis or hydrolysis of the molecules due to temperature or pH (which are the same in the two reservoirs) but also biotransformation (Goring and Hamaker, 1972; Aboul-Kassim and Simoneit, 2000; Matsumura and Murti, 1982). Metabolisation by organisms implies the degradation of organic matter, which is a potential vector of the herbicide load. In the Tarn river, phytoplankton photosynthesis was intense and shallow parts of exclusively Tarn water in Golfech were saturated with oxygen. Mixing with the anoxic water of the Garonne branch of the reservoir where

sediment deposition, anaerobic degradation and methane generation mainly occurs (Gerino et al., 2004) will clearly enrich it with dissolved oxygen (Fig. 4) and could segregate microbial consortia depending on oxygen conditions like in industrial effluent treatment stations.

As indicated, the results obtained for the sediment (<2 mm) are recomposed from the weighted results of the two particle classes: the fine fraction (smaller than 63 μm) made up of clays, silts and colloids and the coarse fraction (between 63 μm and 2 mm) made up of sand and plant remains. Herbicide clearly disappeared from the coarse fraction (Fig. 5) faster than from the fine fraction where it remained detectable. The behaviour with time therefore differs in the different fractions. The reduction of herbicide contamination in the coarse fraction occurred in a regular manner from the entrance to the exit of the reservoir along the main Garonne channel. The Tarn channel is too short to clearly illustrate this phenomenon and so is not presented. Fig. 5 shows that the transformation process, at least in the coarse fraction, is initiated even before the waters mix, in an exclusively Garonne segment — a biologically active shallow-water zone where anoxia is dominant. Herbicide contamination of the coarse fraction seems to be due to plant remains, which can be degraded under these biotic and physico–chemical conditions. However, the absence of atrazine and its major metabolite DEA from the profile suggests that biodegradation is the main explanation.

Likewise, the confluence in Golfech reservoir leads to the sediment being reworked, thus allowing resurfacing of long-term buried sediment. However, the duration of herbicide contamination in the fine fraction is in agreement with the bound herbicide residues in soil.

Guimont (2005) indicated that mechanical reworking of the soil during ploughing leads to desorption of about 18% of the bound herbicide content. A similar process could be proposed for the fine fraction sediment herbicide content during mechanical reworking due to conflicting hydrological regimes, floods, dam flushes or breaching. In this case, extensive herbicide desorption from sediment to water could be feared. The actual occurrence of this potential phenomenon should be more fully investigated.

6. Conclusion

This study presents environmental results confirming herbicide transformation in the lake sediment but revealed much slower kinetics *in situ* than those reported from *in vitro* studies. Reservoirs, which are zones of pollutant accumulation *par excellence*, can fulfil a purifying role depending on their hydrological configuration. When they are placed at a confluence the sediment can be mechanically reworked and, where contrasting conditions occur, support the appearance of dissimilar biotopes and biota ensuring a better transformation capacity from the diversity of the species present.

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