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Urban Impact on Selected Pre-Emergence Herbicides in Sediment cores

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Additional information is available at the end of the chapter

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Abstract

In order to determine if pre-emergence herbicide pollutant source, mixing with many others from residential and industrial activities, has an effect on pollutant degradation, three sediment cores were sampled in appropriate sites of the Garonne river near the city of Toulouse: two in rural surroundings, one upstream and one downstream from the urban area away from its influence, and one downtown close to Toulouse. Atrazine and DEA were analysed and, using DAR pesticide/metabolite ratio, an inferior metabolisation ratio was highlighted in the urban sediment compared to the rural ones, regardless of sedimentation rate, organic carbon content, topography or differences in the intensity of surrounding activities between rural cores.

Keywords: urban area, pesticides, reservoir, metabolites, DEA, atrazine

1. Introduction

Contamination of ecosystems by pesticides, especially aquatic ones, has become a major environmental concern for human health. Ecosystem contamination by agricultural practices and pest eradication procedures has been the subject of many studies, and more recently some have started to outline the impact of urban activities. Blanchoud et al. [1] estimated that 30% of surface water contamination by pesticide was due to applications, mainly of herbicides [2], in urban areas. Research concerning the Mid-Garonne area which was previously presented [2] in order to distinguish agricultural pollution by pesticide from urban one's was highlighted:

Toulouse city (1.100.000 inhabitants) is located in Mid-Garonne basin, surrounded by the third most intensive agricultural area of France, with no significant cities within an 80 km radius. Without topographical restraints, Toulouse city sprawls over the corn plain but the Garonne river flood plain, because of the flood risk, is essentially free of buildings – with the exception of Toulouse city centre.

Most of the herbicides used, excepted glyphosate, belong to s-triazine, substituted urea and anilide families (*inter alia*, for the USA [4] and for Europe [5]). One of their advantages is that some of them can be used for winter treatment in agricultural or urban procedures. However, some molecules such as atrazine have been forbidden since 2003 in France, or are under limitations as substituted ureas, i.e. linuron and isoproturon in the European Community (EC).

The river sediment is well known to be an integrative matrix for organic pollutants of aquatic environments [6,7]. Since there is little variation in the agricultural practice, an accumulation of pesticides is conceivable in river bed sediment caused by the direct agricultural and urban dissolved effluents as well as by the deposition of suspended particulate matter (SPM) contaminated by agricultural and urban use [8–10]. However, accumulation of these molecules is seldom studied in sediment and biota because no reliable and easily implemented method exists. Moreover, herbicide output from sewage treatment plants is estimated as at the same order as herbicide input [11]. Sewage treatment plants are mainly inefficient for retaining such molecules, with an intermediate hydrophobicity, i.e. $\log K_{ow}$ between 2 and 3.5, because of the use of standards appropriate to more hydrophobic molecules. Thus, pesticides will be insufficiently retained – like other pollutants with the same order of hydrophobicity, such as pharmaceuticals. Such antibiotic molecules could have an inhibiting effect on bacteria's activity [12], and monitoring such a flux could be a challenging target because of the molecules' number and their diversity and because of the fugacious but significant input events as consummation mode or storm water.

The aim of the present study is to determine the inhibiting conditions prevailing in urban sediment by following the pesticide biodegradation activity. Instead of monitoring chemical inputs for which the microbial inhibition is a multifactorial phenomenon crossing several contingencies [12,13], the authors focused on the pesticide/metabolite ratio or DAR ratio, considered as the result of such inhibitive conditions. In other fields, Adams & Thurman, [14] considered the DEA/atrazine ratio as the evidence of groundwater mobility. Based on Aelion & Mathur [15], crossing DAR with degradation activity, the authors will investigate the relationship between urban context and the organic chemical degradation.

Taking account of previous studies [3, 16–18], atrazine will be used because of its suitable extraction method for sediment [3], proven ubiquity in the Mid-Garonne River and the well-known relationship between atrazine and its metabolite desethylatrazine (DEA). The authors assume that deisopropylatrazine (DIA) is mainly due to low- O_2 conditions but, as previous studies indicated significant DEA concentrations in the sediment core, the DIA concentrations were not taken into account as uncertain. Moreover, atrazine is degraded in DEA under oxic conditions, corresponding to sediment surface layers. Due to their half-lives and K_{ow} , it is not consistent to consider deeper layers' degradation impacted by early diagenesis, bioturbation and sediment cementation [19,20].

2. Material and methods

2.1. Sampling sites and period

Using sediment cores, the authors have sampled three sites – one corresponding to an urban area near the Toulouse sewage sludge output into the Garonne River, two corresponding to agricultural areas, respectively, upstream and downstream of Toulouse city, at a geodesic distance about 40 km (Figure 1).

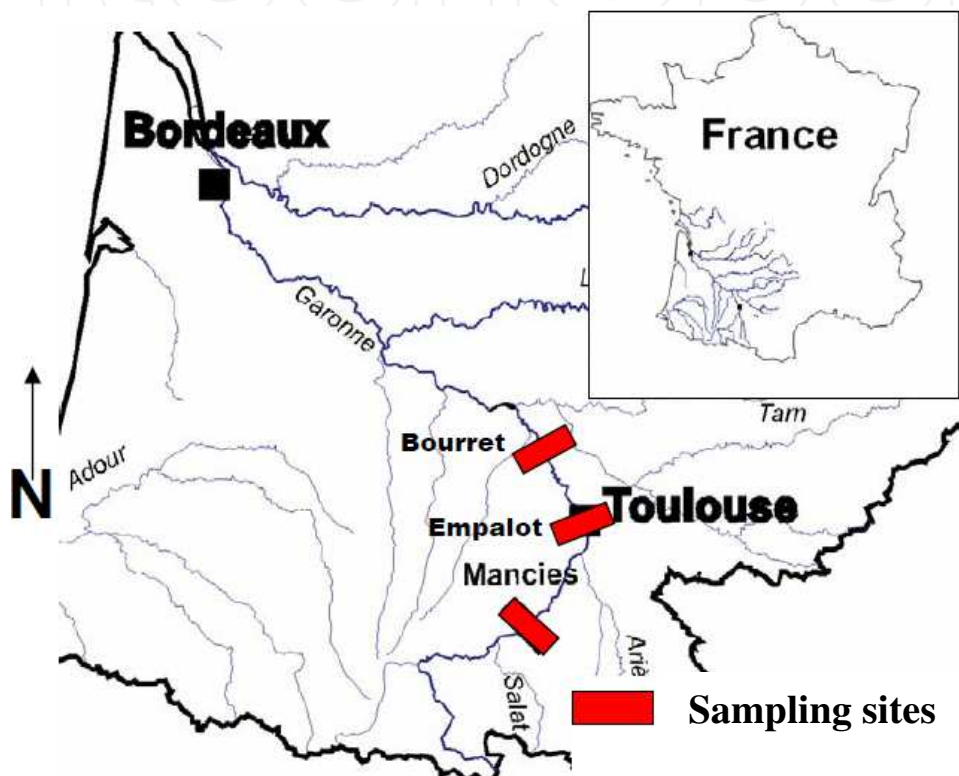


Figure 1. Map of sampling sites. Bourret and Mancies are 40 km geodesic distant from Toulouse.

Empalot weir is near Toulouse city downtown. This site was previously accurately investigated [21]. Suitable sedimentation characteristics and sedimentation rate were estimated about 0.41 cm/year by Devault et al. [18]. The first mention of Empalot weir dates from the Middle ages (1183 A.D.) because the weir was erected simultaneously with the Château Narbonnais's flour mill. The last 100-year flood (1900 A.D.) destroyed its deck which was rebuilt in 1922 A.D simultaneously with Ramier's hydropower station building.

Mancies dam, also named Carbonne dam, is a conventional hydropower one, which regulates the Garonne river's flow upstream from Toulouse city since 1965 A.D. This place was studied and described elsewhere [17]. Mancies dam is located at the boundary of the ancient regions of Volvestre and Comminges known for corn cultivation and a progressively predominant animal husbandry going towards the Pyrenees: upstream from Toulouse, no significant town lies on banks of the Garonne. At the coring place, sediment rate was estimated about 1.23 cm/

year [18]. Drinking water for the Toulouse urban area is drawn from the Garonne river close to the dam downstream.

Bourret oxbow is located about 80 km downstream from Toulouse city. Investigated by Steiger et al. [22] and Vervier et al. [23], in a conserved section of the Mid-Garonne, its sedimentation rate is especially low, about 1 mm/year, because of the topographic buffering of Garonne river flows. Indeed, Bourret oxbow is mentioned since 18th century. Riparian forest is 2-km-wide there at the thinnest place, but Bourret oxbow coring place is located at the meeting point between Garonne stream and the outlet of the 5-km-long oxbow lake, parallel to Garonne river but close to intensive agricultural Mid-Garonne activity – wheat and maize predominate. Nutrient and trace metal data elsewhere [24] highlight the limited urban impact on this site.

Sediment samples were collected during the winter low-water event corresponding to the beginning of herbicide application and to maximal sedimentation. The most marked low-water event of the winter was chosen. Thus, the sediment collected had never been above water level – consistent information mainly for Bourret station. Water temperature during winter was always about 5°C – a propitious temperature for pesticide degradation. The intensity of pesticide use in March corresponds to the annual average spreading level of pesticides.

2.2. Sample treatment

The cores were cut into sections: Section 1: 0 to 2 cm, Section 2: 2 to 6cm, Section 3: 6 to 14 cm, in order to monitor the 0–14 cm deep sediment surface layer where early diagenesis occurs [25]. Section 29 to 31 cm deep for all sites and Section 44 to 46 cm deep were also added except for the Empalot site.

For all layers, the different sediment fractions were separated according to the methods recommended by the Commission of Oslo and Paris (OSPAR). The components of the dried sediment were separated in an agate mortar and sifted with a 2 mm mesh (stainless steel sieves from Retsch GmbH and Co. KG (Haan, Germany)) to distinguish and eliminate coarse plant remains and gravel. In practice, coring was performed in sediments known to be free of large obstacles.

Total organic carbon content, due to organic matter, was estimated with a Leco CS 125 (St Joseph, Michigan). Conventional Kjeldhal method was used for organic nitrogen analysis on a Foss Analytical A/S's Tecator Kjelec-auto 1030 analyzer line (Hillerød, Denmark). Carbonate was estimated using Bernard's calcimeter.

2.3. Pesticide assay

2.3.1. Sample analysis

All solvents were of analytical grade for pesticide analysis ("Pestipur" by SDS, Peypin, France). Analytical grade anhydrous sodium sulphate was also from SDS. Pesticide standards (Mix 44) prepared by Dr. Ehrenstorfer GmbH (Augsburg, Germany) were purchased from CIL, Sainte-Foy-la-Grande, France. Reference soil (Eurosoil7) was from Sigma-Aldrich (St Louis, Missouri,

USA). Florisil cartridges used for purification were from Waters Corporation (Milford, Massachusetts, USA).

The protocol used is described in detail elsewhere [3]. Extraction was performed with a Dionex Accelerated Solvent Extractor (ASE 200) (Dionex, Salt Lake City, Utah, USA). Diatomaceous earth (Hydromatrix®) was from Varian, Palo Alto, California, USA. ASE extracts were analysed using HP5980 Series II gas chromatograph coupled to an MSD HP5971 mass detector (Agilent, Santa Clara, California, USA). Chromatographic conditions in the splitless mode (injection temperature: 280°C) were set up at an initial temperature of 45°C. The first step had a temperature increase rate of 35°C/min up to 180°C then the second step at 8°C/min up to 280°C and, finally, a 10 min plateau at 280°C. The detection conditions were temperature 300°C and EMV 2600V.

Limit of detection and limit of quantification are respectively 0.0001 and 0.001 µg/g.

3. Results and discussion

DEA pollution prevails in the three cores (Table 1) and especially in the fine fraction one (Figure 2): the metabolite is detectable and quantifiable for all samples in fine fraction and is only not detectable or quantifiable for the two Bourret's layers in coarse one. Inversely, atrazine is mainly undetectable (15 undetectable concentrations for 28 samples) – even if detection limits were similar for the two molecules.

	Fine fraction						Coarse fraction				
	Depth (cm)	Silts and clays (%)	TOC (%)	Renfield ratio	DEA (µg/g)	Atrazine (µg/g)	Sands and gravels (%)	TOC (%)	Renfield ratio	DEA (µg/g)	Atrazine (µg/g)
M1	0–2	91,2	2,7	8,20	0.07	0.26	1,2	6,57	15,63	T	0.02
M2	2–6	95,6	3,4	10,84	4.18	0.35	3,7	6,68	16,52	0.01	0.01
M3	6–14	94,5	4,3	11,98	0.43	0.81	7,2	8,35	18,12	0.01	0.01
M4	29–31	97,9	3,5	11,71	1.29	-	3,2	14	18,68	T	-
M5	44–46	98	2,60	10,95	0.02	0.01	6,6	3,97	15,07	0.01	T
E1	0–2	60,8	4,1	15,12	0.77	-	39	1,45	16,72	0.01	-
E2	2–6	73,2	2,8	10,20	5.44	0.31	27	1,41	14,11	0.05	0.13
E3	6–14	63,7	2,3	10,31	0.33	0.18	36	1,51	15,92	0.05	-
E4	29–31	52,8	1,8	9,76	-	0.20	47	1,25	13,83	0.02	0.02

	Fine fraction						Coarse fraction				
	Depth (cm)	Silts and clays (%)	TOC (%)	Renfield ratio	DEA ($\mu\text{g/g}$)	Atrazine ($\mu\text{g/g}$)	Sands and gravels (%)	TOC (%)	Renfield ratio	DEA ($\mu\text{g/g}$)	Atrazine ($\mu\text{g/g}$)
B1	0–2	94,1	2,2	8,91	22,37	-	5,9			T	-
B2	2–6	90,6	2,2	11,40	0,85	-	9,4	1,79	8,78	-	-
B3	6–14	82,1	0,66	12,83	0,38	0,07	18	1,71	4,78	0,02	-
B4	29–31	41,3	1,8	10,29	0,04	-	59	0,31	10,29	0,03	-
B5	44–46	29,3	1,6	12,35	0,08	-	71	0,33	12,35	0,11	-

Table 1. DEA and atrazine profiles ($\mu\text{g/g}$), granulometric data and total organic carbon content (%) and Renfield ratio (C/N, dimensionless) from Mancies (M), Empalot (E) and Bourret (B) sampling sites. Sedimentation rates are respectively estimated about 0.1, 0.41 and 1.23 cm/year.

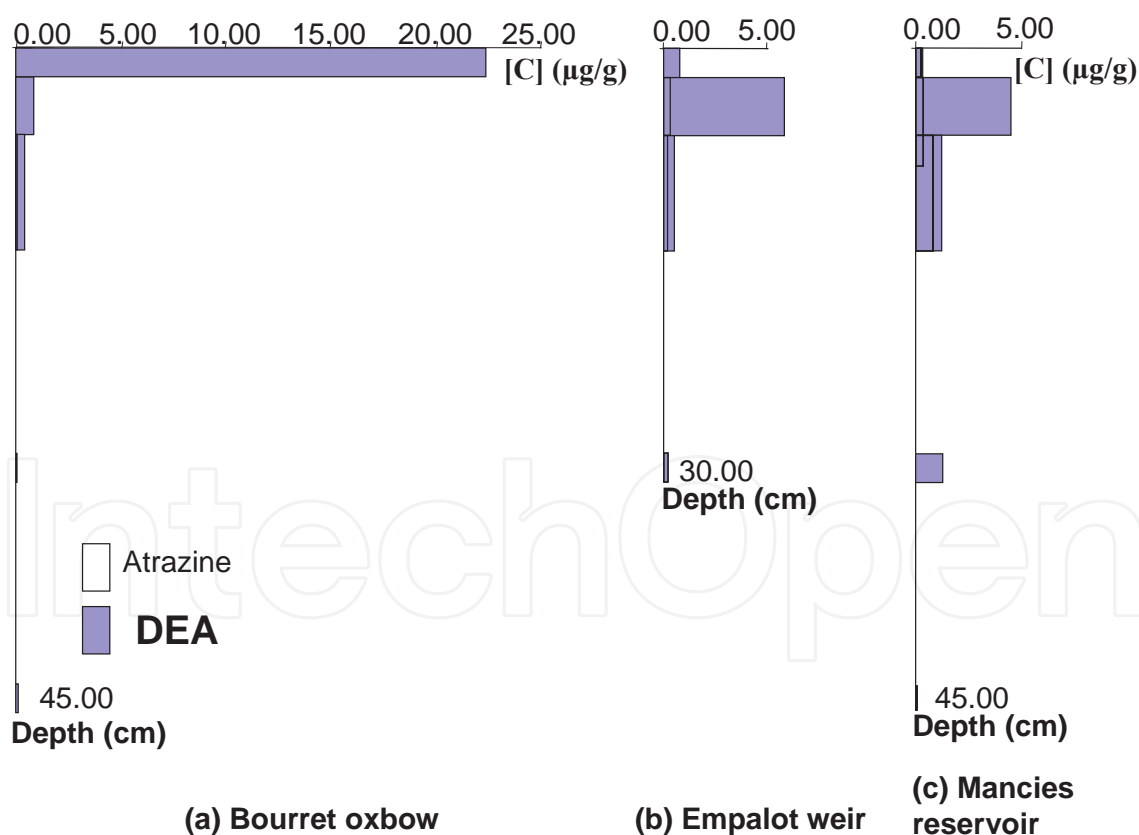


Figure 2. Representation of the contamination of the fine fraction in (a) Bourret oxbow, (b) Empalot weir and (c) Mancies reservoir. Sedimentation rates are respectively estimated about 0.1, 0.41 and 1.23 cm/year.

Bourret oxbow surface layer is the most polluted layer (22.37 $\mu\text{g/g}$). Such concentration, even after considering all the core samples, argues that Bourret is the most polluted site (2.97 $\mu\text{g/g}$) even if atrazine concentration is only detectable or quantifiable for one sample, at 6–14 cm. Fine fraction surface layer, i.e. 0–2 cm deep, represents about 86.4% of total DEA stock from the core; 6–14 cm layer presents a significant contamination by atrazine – even it is the only one sample from Bourret where atrazine contamination is detected or quantified. At such depth, the authors hypothesize that bioturbation could be evoked: even if no evidence of benthic animal terrier was found, it could explain such an isolated result because the whole core allowed hypothesizing an oxyd atrazine degradation in the surface layer.

The core sampled in the Empalot urban weir presents an average concentration of about 1.75 $\mu\text{g/g}$; DEA contamination of the fine fraction is the least important compared to the other sites: non-DEA from fine fraction contamination represents 27.6% of total contamination of the whole core. Atrazine and its metabolites have sensibly the same proportion in the coarse fraction (0.41 $\mu\text{g/g}$ for DEA, 0.36 $\mu\text{g/g}$ for atrazine).

The contamination of the core sampled in the Mancies reservoir is globally limited to DEA pollution of fine fraction. Contamination by coarse fraction is minor compared to the DEA one (12.6%), with an intermediate score regarding the two others sites. Like the coarse fraction from the Empalot urban weir, atrazine and DEA presented similar average concentration (0.01 $\mu\text{g/g}$ for each) but, by contrast to the Empalot site, concentrations observed are scarce and low, limiting the interpretation.

3.1. DEA/Atrazine Ratio (DAR)

DEA/atrazine molar concentration ratio could be used for groundwater pollution (DAR) [14,26–28] in order to determine point source from non-point source contamination and the timing and movement of atrazine in reservoirs and streams. For sediment, DAR was used for degradation investigation [15]. However, sediment variability depending on origin, transport, periodical or local pesticide uses (*inter alia*, [29–31]), needs to be pondered. Moreover, because of undetectable or unquantifiable concentrations, the choice of a substitutive value, in order to avoid division by zero, could be a critical parameter, which needs to be buffered. In the present case, detectable but unquantifiable concentrations were estimated at 0.005 $\mu\text{g/g}$, corresponding to the half of quantification limit, and undetectable concentrations were estimated about 0.001 $\mu\text{g/g}$.

In the present case, authors proposed to compare DAR performed for the fine fraction by DAR performed for coarse fraction.

Comparing average DAR for fine fraction (aDAR_{ff}) to average DAR for coarse one (aDAR_{cf}) provides a notable similarity between rural sites, as opposed to strictly urban areas.

3.2. Statistic study

Non-parametric Spearman's rank correlation test has been performed, considering the variable natures. In order to have the same number of observations i.e. chemical concentration in

sediment, for each variable, i.e. cores or fractions, the deepest layer for the Bourret and Empalot sites were excluded.

The statistic study should first test the independence between DEA concentrations and atrazine ones and signals an independence for all the cores at $\alpha = 0.05$ (even $\alpha = 0.1$) for $n = 8$, incidentally justifying DAR use for sediment.

The second step seeks to determine if coarse fraction and fine fraction contaminations are dependent.

If the three site datasets confirm the dependence between coarse and fine fraction, both for atrazine and for DEA, the relationship between coarse and fine fraction characterises the Bourret and Mancies cores: $\alpha = 0.05$ for $n = 8$ each for their superior dependence; for Empalot core: $\alpha = 0.5$ (and not 0.05) for $n = 8$ lacks pertinence. Moreover, a striking similitude between Bourret and Mancies data appears: respective r_s are extremely close (0.53 each).

Such results are found when cores are compared: similarity between Mancies and Bourret is quite obvious ($\alpha = 0.005$ for $n = 16$) while similarity is seen between the Empalot core and the other ones but at a lesser scale, i.e. with $\alpha = 0.05$ (and not 0.005) for $n = 16$. r_s obtained when comparing Empalot to Bourret and then Empalot to Mancies were also close, highlighting the similitude between Mancies and Bourret cores.

3.3. Urban chemical mix impact on atrazine biodegradation

Considering statistical results, the authors propose to compare DAR obtained with the fine fraction to DAR obtained with the coarse one (1) since the fractions are not dependent, as the previous statistical analysis shows, (2) atrazine degradation is due to fine fraction which collects chemicals associated to organic matter, i.e. silts, clays and humic acids [32], and (3) because coarse fraction contamination is not due to contamination of lignin-rich allochthonous organic matter as the Renfield ratio shows (Table 1), and to use average concentration for DAR calculation, because of unquantifiable or undetectable samples. Authors followed equation (1):

$$\frac{\{[\text{DEA}]/[\text{Atrazine}]\}_{\text{ff}}}{\{[\text{DEA}]/[\text{Atrazine}]\}_{\text{cf}}} \quad (1)$$

where [DEA] and [atrazine] are the average concentrations observed in DEA and atrazine in the fine fraction (ff) is the numerator and coarse fraction is the denominator, for each core. For Bourret and Mancies, DAR ff/cf provides an obviously close result: 141 for each. Empalot's one is about 13 (Table 2).

Such a ratio could be justified by the lower degradation observed in the whole core, especially comparing Bourret and Mancies sedimentation rates (1 vs 12 mm/year), chemical vertical profiles and contamination levels (mainly in surface layer for the first and mainly in 6–14 cm for the second).

	DARff	DARcf	DARff/DARcf
CM1	0,27	0,25	1,08
CM2	11,94	1,00	11,94
CM3	0,53	1,00	0,53
CM4	1290	5,00	258,00
CM5	2,00	2,00	1,00
Average Mancies	260,95	1,85	141,05
E1	770,00	10,00	77,00
E2	17,55	0,38	45,63
E3	1,83	50,00	0,04
E4	0,01	1,00	0,01
Average Empalot	197,35	15,35	12,86
B1	22370,00,	5,00	4474,00
B2	850,00	1,00	850,00
B3	5,43	20,00	0,27
B4	40,00	30,00	1,33
B5	80,00	110,00	0,73
Average Bourret	4669,00	33,2	140,64

Table 2. DAR depending granulometric fraction. DARff (dimensionless) correspond to fine fractions and DARcf for the coarse one.

Considering layer thickness and normalizing DEA and atrazine concentration like Koelmans et al. (1997) proposed (2), the result is still more obvious: Mancies and Bourret ratios stay close (respectively 117 and 145) compared to Empalot's one (about 4).

The main similarity between Bourret and Mancies is the surrounding rural landscape, limiting chemical pollution to that of agricultural activity: pesticides. It is obvious, moreover, that the pesticide level, considering atrazine, DEA or other pesticides [3, 16] is very similar to Empalot. Such difference, characterised by the lack of atrazine degradation, could be imputed to three sources:

- An input of contaminated fine fraction due to sewage sludge or sewer system. It is not a non-sense considering the works of Jiang et al. [33] and [34] inform us that pyrethroid adsorption on concrete is rapid, i.e. 85% and more of pyrethroids are adsorbed in the early days, and concrete undergoes structural deteriorations, providing possibly polluted concrete particles during rain wash-off events to surface water system. Consequently, pesticide transfer by runoff from concrete (between 30% and 60% in-lab transfer rate [35]) is mainly due to solid particles and not due to dissolved molecules whose size introduces them into fine fraction. It could justify why hydrophobic pesticides like atrazine and DEA

are more prone to wash-off than glyphosate from cement slab – but carbon organic content does not strengthen this hypothesis.

- A lack of degradation due to early diagenesis difference leading to the proposal of two hypothesis: (1) minor oxygenation in urban water compared to rural ones, but there is no evidence of it. Inversely, wastewater plant effluents are monitored and any significant clue support such hypothesis in dataset collected in situ or in sewage treatment actors. Moreover, the Empalot area was in detail studied elsewhere [21] during a period of less efficient effluent treatment compared to the authors' core sampling. Moreover, temperature of water was low, enhancing oxygen saturation content. (2) Difference in bioturbation activity – knowing that bioturbation, at global scale, prevails on abiotic early diagenesis [35]. There is no evidence of this, either in chemical profile or in the organic matter content: the lone example of possible bioturbation is in the core from Bourret.
- Metabolic brakes, leading to reduced atrazine biodegradation. Such phenomenon has never been previously demonstrated using pesticide/metabolite ratio even if [15] used DAR on polluted sediment and Harrison et al. [36] highlighted the site impact on microbial activity. In the present case, in similar conditions between urban and rural sites, the authors suggest that the lower metabolic yield highlighted by DAR_{ff}/DAR_{cf} ratio could be due, at least partially, to the chemical mix typical of the urban area, especially because of antibiotic micro-pollution [37].

The present study should be completed in order to compare microbial activity in sediment influenced by urban mix of urban and agricultural activities, even if:

1. degradation gene estimation [38] is not necessarily an alternative factor able to supersede DAR – in this case, *tfdA* gene, coding for MCPA mineralization, was more pronounced in MCPA pollution even if mineralization rate, influenced by organic carbon content, finally favours agricultural soil as bioavailability favours urban ones.
2. Global degradation activity, monitored by labile organic matter, has been performed with sucrose, without providing significant differences. Such a molecule is acutely degradable, when atrazine could differ following enzymatic diversity and, likewise, early diagenesis conditions [39], which characterise microbial sediment environment [19], were not reproduced, nor urban water dissolved chemical mix. In the present case, sucrose metabolism seems to be too rapid, for each sediment, for a valid interpretation – when atrazine degradation takes months in soil, and significantly longer in sediment [16].

4. Conclusion

Even if sedimentation rate, organic carbon content, topography or surrounding activities' intensity differ, inducing significant differences between cores from Bourret and Mancies, such samples from rural areas differentiate themselves clearly from the urban core from Empalot weir. This last one presents a less degraded level of atrazine in DEA, which could be attributed to chemical mix, including antibiotics. In this way, and while waiting for further data, the

authors hypothesize that the vertical profile of DEA and atrazine is impacted by urban chemical mix from the Toulouse area, limiting atrazine metabolisation and leading to atrazine accumulation in a sediment core.

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