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1 **Multivariate tiered approach to highlight the link between large-scale**
2 **integrated pesticide concentrations from POCIS and watershed land-uses**

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4 Marion Bernard^a, Sebastien Boutry^b, Robin Guibal^c, Soizic Morin^b, Sophie Lissaldec, Gilles
5 Guibaud^c, Margaux Saüt^d, Jean-Pierre Rebillard^e, Nicolas Mazzella^{b*}

6
7 ^a SGS Life Science Services, 90 Av. des Hauts de la Chaume BP 28, 86281 Saint-Benoît

8 ^b Inrae, UR EABX, 50 Avenue de Verdun, 33612 Cestas, France

9 ^c Université de Limoges, E2Lim, 123 Avenue Albert Thomas, Limoges, Cedex 87060, France

10 ^d DREAL Occitanie, 1 Rue de la Cité Administrative, 31000 Toulouse

11 ^e Agence de l'Eau Adour-Garonne (AEAG), 90 Rue du Feretra, 31078 Toulouse CEDEX 4, France

12
13 *** Corresponding author at: Inrae, UR EABX, 50 Avenue de Verdun, 33612 Cestas, France**

14 **E-mail address: nicolas.mazzella@inrae.fr**

16 **ABSTRACT**

17 This paper describes an automatized multi-step methodology in order to identify the
18 relationships between integrative pesticide quantifications and land-use on a given watershed.
19 This methodology contains multivariate statistical analyses such as hierarchical cluster
20 analysis (HCA) and principal component analysis (PCA), which are commonly used for the
21 interpretation of complex geospatial datasets. A large amount of pesticide concentration data
22 were collected along 1-year monitoring in 2016, for 50 sites located on the Adour Garonne
23 basin (South-West France). For those sampling sites, concentrations of 37 selected pesticides
24 were investigated during six periods of 14-days immersion of integrative samplers.
25 Specifically, the sampling devices used were Polar Organic Chemical Integrative Sampler
26 (POCIS), providing time-weighted average concentration estimates. For each studied site, the
27 associated watershed and its land-use repartition were determined based on the Corine Land
28 Cover 2012 and geographical information system (GIS) aggregation of data. The HCA
29 clustered the 50 sites into five groups with similar main land uses. After that, the datasets of
30 pesticide integrated concentration and land use repartition were analyzed in a PCA. The key
31 variables (pesticide distribution and concentrations) responsible for sampling site
32 discrimination showed consistent patterns of distribution with specific land uses. In order to
33 confirm these observations, pesticide fingerprints (based on the waffle method) of sites with
34 contrasted land use relative to the surface areas were compared. These fingerprints confirmed
35 that there was different and specific patterns, visible at a glance, of pesticide occurrence in
36 surface water, in relation with their initial use at the catchment level. This method allowed
37 identifying sources of contamination that could be interesting to prevent or contain pesticide
38 pollutions beyond simply acting on the most at-risk areas.

39

40 Keywords: passive sampling, pesticides, multivariate analysis, river catchments, tiered
41 methodology

42 1. Introduction

43 The use of organic pesticides in an agricultural or non-agricultural context leads to the
44 contamination of the aquatic environment. This anthropogenic influence has an impact on
45 aquatic ecosystems, and also human beings. Within this frame of reference, monitoring
46 networks are performed in order to evaluate the water quality for pesticides. These networks
47 acquire each year large amounts of data (*e.g.* monthly pesticide concentrations). These data are
48 usually compared to regulatory thresholds such as those from the Water Framework Directive
49 (WFD ¹) in order to evaluate the quality of water bodies, and highlight the vulnerable and
50 degraded areas. In addition, these data could be used to identify the impact of human activities
51 regardless of their intensity. This means finding a way to identify sources of contamination for
52 implementing corrective actions to prevent pesticide pollutions on the most at-risk areas.
53 However, accessing this type of information with a large amount of data collection can be
54 time-consuming and laborious.

55 A study performed by Macary, et al. ² used the agricultural pressure (land use, farmers
56 practices) of different size watersheds and soil characteristics relating to the environmental
57 vulnerability of the surrounding surface water environment (slope, pedology of agricultural
58 parcels...) to establish an indicator of pesticides contamination risk (Phytopixal method). With
59 this multi-criteria method, the authors proposed cartographic projections of the pesticides
60 contamination risks for the studied watershed (*i.e.* the Coteaux de Gascogne, South-West of
61 France). Another study performed by Morin, et al. ³ on the same watershed demonstrated that
62 the mapping of pesticide contamination risk with the use of the Phytopixal method allowed
63 obtaining a relevant estimate of pesticide real exposure *in situ* (*i.e.* correlated with pesticide
64 concentration measured), and further assessment of toxic impacts on the diatom communities
65 in the Neste river system. Several other studies using multivariate statistical analyses
66 (hierarchical clustering and/or principal component analysis) were successful in establishing
67 links between surface water chemistry (*e.g.* nutrients, trace elements, pesticides) and land uses
68 ⁴⁻⁸. In the latter studies, grab sampling was used to describe surface water contamination by
69 chemicals. However, this sampling strategy provides data with a lack of temporal
70 representativeness since it corresponds to a point-in-time snapshot, and then contamination
71 fluctuations could be missed ⁹⁻¹⁰. Thus, with the aim of establishing relationships between
72 global estimates of land use (low temporal resolution) and overall water quality, integrated
73 measurements of water quality would likely improve correlations over spot samplings.

74 In our study, an alternative sampling approach which corresponded to the use of passive
75 samplers was performed. This sampling strategy which consists of immersing a device in
76 water for a fixed period allows the *in situ* pre-concentration of target compounds, and then
77 provides a time weighted average concentration (TWAC) with integration of contamination
78 fluctuations¹¹⁻¹². For 50 sites located on the river of the Adour-Garonne Basin (South-West of
79 France), the concentrations of 37 selected pesticides were investigated during six periods of 14
80 days spread over the year 2016, by the use of the Polar Organic Chemical Integrative Sampler
81 (POCIS). POCIS are widely used for the sampling of moderate polar pesticides with $0 < \log$
82 $K_{ow} < 4$ ¹³. Due to TWAC estimates obtains, such passive samples allows an increase of both
83 number of quantified pesticides and detection frequencies compared to grab sampling¹⁴⁻¹⁸. In
84 addition, large-scale spatial and temporal trend studies demonstrated that complex mixtures
85 of pesticides accumulated by passive samplers can be well correlated with land use¹⁹⁻²⁰.

86 By using the large amount of pesticide data collected during this one year monitoring, a visual
87 and automatized methodology was proposed in order to link pesticide contaminations of river
88 waters and watershed land uses. To do that, information on land use of each catchment area
89 containing the various sampling sites was determined from Corine Land Cover 2012. Land
90 uses and pesticide datasets were analyzed against each other with multivariate statistical
91 methods, such as hierarchical cluster and principal component analysis. Furthermore,
92 pesticide fingerprints of each sampling sites was established by using “waffles”. Finally, this
93 study aimed to propose a tiered methodology in order to highlight the most threatened areas
94 and periods in terms of pesticide contaminations.

95 **2. Materials and methods**

96 **2.1. Data acquisition**

97 *2.1.1. Study area: the Adour-Garonne basin*

98 The Adour-Garonne basin is located in the southwest of France and covers an area of 117,650
99 km². It is composed of 116,817 km of rivers and of a coastline strip of 650 km. This basin has a
100 population of *c.a.* 7,000,000 inhabitants with pronounced rural character (30 % of the
101 population), 35 cities with more than 20,000 inhabitants each (28 % of the population) and two
102 metropolises (Toulouse and Bordeaux) with *c.a.* 750,000 inhabitants each. Concerning its land
103 use, and according to the Corine Land Cover 2012 (CLC 2012), 55 % of the basin’s surface area
104 corresponds to agricultural areas (*i.e.* crops, vineyards, orchards...) and 40 % to forest areas
105 (Figure 1). The remaining 5 % are divided between artificial areas (*e.g.* urban, industrial areas),

106 wetlands (*e.g.* marshes) and water surfaces (*e.g.* lakes). For this study, 50 sampling sites from
107 the Water Framework Directive network were selected. These sampling sites (Figure 1) were
108 characterized by a diversity of land uses, implying different water pesticide contamination
109 profiles ¹⁴.

110 2.1.2. Pesticides quantification in surface water with POCIS

111 The 50 selected sites within the Adour-Garonne basin were sampled during 6 periods of 14
112 days evenly distributed between March and December 2016 by the use of passive samplers, in
113 order to obtain pesticide contamination levels. In this study, the Polar Organic Chemical
114 Integrative Sampler (POCIS) was used in his “Pharmaceutical” configuration ^{13, 21}. With this
115 sampler, 37 neutral and moderately polar pesticides ($0.57 < \log K_{ow} < 4.14$) were investigated.
116 These 37 selected compounds (Table 1) included different chemical families (*e.g.*
117 chloroacetamides, ureas, etc.) and biological activities (*i.e.* herbicides, fungicides, insecticides,
118 as well as their respective known metabolites) in order to cover a large range of treatments.
119 All the sample processing and analyses were described in Bernard, et al. ¹⁴. Briefly, before their
120 field deployment, POCIS were prepared at the laboratory with 200 mg of Oasis HLB sorbent
121 (30 μ m particle size, 810 m²g⁻¹, divinylbenzene *N*-vinyl-pyrrolidone, Waters, France) enclosed
122 between two microporous polyethersulfone membranes (PES - 90 mm diameter and 0.1 μ m
123 pore size, PALL[®], VWR, France) and compressed by two holder washers. After the exposure
124 period, POCIS were disassembled and the pesticides were extracted from the sorbent with 3
125 mL of methanol then 3 mL of methanol:ethyl acetate 75:25 (v/v). The 6 mL extract obtained
126 was evaporated with a Speedvac system (1h30 at 60°C - Thermo Fisher Scientific, France) after
127 adding 10 μ L of internal standards. Before analysis, the samples extract was reconstituted with
128 1 mL of ultrapure water:acetonitrile 90:10 (v/v). The analysis of pesticides from POCIS was
129 performed with two liquid chromatography apparatus coupled with high-resolution mass
130 spectrometry (*i.e.* HPLC-MS/MS and UHPLC-Q-ToF). For the both analytical methods, the
131 compound-dependent instrumental quantification limits (IQL in μ g L⁻¹) were determined with
132 method validation (NF T 90-210, AFNOR ²²) and grouped in Table S 1. In addition and
133 according to the method of Poulhier, et al. ¹⁸, the compound and analytical technique dependent
134 quantification limits for POCIS (QL_P in μ g L⁻¹) were calculated and also grouped in Table S 1.
135 For each sampling site and period, POCIS analysis provided a time-weighted average
136 concentration of each pesticide in water (\overline{C}_w in μ g L⁻¹). At last, this 1-year pesticide monitoring
137 provided a large amount of data, which was equal to 11,100 water data on pesticide
138 concentrations acquired (*i.e.* 50 sites \times 6 periods \times 37 pesticides).

139 2.1.3. Preparation of the pesticide datasets

140 Because of the large amount of data collected, a rigorous and automatized data preparation
141 methodology was implemented. In this study, the raw data was composed by the pesticide
142 concentrations measured in the POCIS receiving phases (C_{POCIS} in ng per POCIS) after their
143 field deployment. These concentrations were grouped in the same database for all stations,
144 campaigns and pesticides. Then, these raw data followed the processing described in Figure S
145 1, which was performed with two software programs: Microsoft Excel (version 14.0.7212.5000)
146 and R software (R Core Team, 2017). This preparation step was essential to check the data
147 before their use in the methodology development. Firstly, they were sorted according to the
148 IQL (in $\mu\text{g L}^{-1}$ - Table S 1) and normalized by the mass of the receiving phase recovered inside
149 the POCIS ($M_{\text{Sor bent}}$ in g) to obtain C_{POCIS} in ng g^{-1} . Second, the time-weighted average
150 concentrations (\overline{C}_w in $\mu\text{g L}^{-1}$) of each pesticide in water were calculated as described in Bernard
151 et al. (2019), and then sorted with the QL_P (in $\mu\text{g L}^{-1}$, Table S 1). Afterwards, quantification
152 frequencies (QF in %) for each studied pesticide ($n = 37$) and for all stations and periods
153 combined were calculated (*i.e.* annual QF). When annual QF was lower than 10 %, the
154 compound was removed from all the dataset, because contamination levels measured were
155 not significant and these variables provided no discrimination power between water qualities
156 from different locations, in contrast to other compounds with higher QF. This approach also
157 allows ensuring robustness of statistical treatments by removing substantial noise from the
158 analysis. After this step, the number of studied pesticides or metabolites decreased from 37 to
159 23 (Table 1). Consequently, the total number of data was reduced to 7038 \overline{C}_w values in $\mu\text{g L}^{-1}$.

160 2.1.4. Data analysis / methodology developed

161 The methodology developed was adapted from several studies that used multivariate analyses
162 to better characterize the sources of water chemicals contamination^{4-5, 7-8}. Because of the large
163 amount of data collected, their processing and interpretation are often difficult. In this context,
164 multivariate statistics are useful approaches since they decrease the number of components in
165 a complex dataset by identifying key variables responsible for patterns of sampling sites²³.

166 2.1.5. Site classification based on watershed land use.

167 For each site, the associated watershed was determined using the GRASS plugging and QGIS
168 software (version Las Palmas 2.18). To do that, the "r.water.outlet" function was used to delimit
169 the watershed using the outflow coordinates and the digital elevation model (DEM). Then, the
170 area of each watershed was calculated. At last, the percentages of land uses of each watershed

171 were evaluated by making an intersection between the CLC 2012 layers (pixel size: 500 m * 500
172 m) and the determined watershed. All the sampling sites information is available in Table 2.

173 A hierarchical cluster analysis (HCA) was performed on the site data in order to identify
174 groups of sites that had similar land use profiles. A classification scheme using the Euclidean
175 distance for similarity measures between percentages of land use was performed. The Ward's
176 method was used for the establishment of the links between sites to improve distinctive power
177 of the classification ^{8,24}.

178 *2.1.6. Relationships between water pesticides contamination and watershed land use.*

179 In an effort to show the relationships between quantified pesticides and land use at the
180 sampling site, principal component analyses (PCA) were performed on the pesticides
181 concentrations measured for each site and period, after standardization of the POCIS data ($\overline{C_w}$
182 in $\mu\text{g L}^{-1}$) by a Yeo-Johnson transformation ²⁵. This transformation accounted for the high
183 variability of the contamination levels between sites, periods and compounds ^{14, 18, 26} and
184 reduced the influence of extreme values on variance ²³. Moreover, the data transformed this
185 way achieved a normal distribution, which is required to conduct this multivariate statistical
186 analysis ²⁷. In this analysis, the 23 studied pesticides were considered as variables, and
187 individuals corresponded to each sampled site at each period (*i.e.* period-station code).

188 The axes extracted from the PCA performed with the contamination levels measured ($\overline{C_w}$ in
189 $\mu\text{g L}^{-1}$) for the 23 studied pesticides and all periods (n=6) and sites (n=50) were then rotated
190 with the Kaiser Varimax criterion²⁸ in order to enhance the interpretation. This Varimax
191 rotation makes it possible to bring the groups of variables closer to the axes that allow
192 obtaining a better evaluation of their contribution, by associating a limited number of factors
193 to each variable. The correlation between the variables (*i.e.* pesticides) and the defined axes are
194 expressed by the loadings (or eigenvalues). For each axis and variable, these loadings were
195 grouped in Table S 2 and allowed highlighting the most discriminating variables.

196 At last, site groups obtained with HCA based on land use were projected on the PCA two
197 dimensional plots in order to picture rough correlations between quantified pesticides and
198 sampling sites (land use).

199 *2.1.7. Specific pesticide fingerprint and relationship with land use.*

200 To go more in depth in understanding and visualizing the relationships between land use and
201 pesticides contamination, sites exhibiting specific profiles based on the PCA were focused on.
202 Specifically, sites with contrasted profiles (forest, agriculture, and vineyard) were selected. The

203 seasonality and magnitude of pesticide contamination profiles were illustrated using the
204 “waffle” method²⁹. These multivariate analyses and the pesticides fingerprint were performed
205 with R Software (R Core Team, 2017), packages “ade4”³⁰, “adegraphics”³¹ and “cluster”³² ;
206 the waffles were drawn using “ggplot2”³³ and “treemapify”³⁴ packages.

207 **3. Results and discussion**

208 3.1. Site classification based on the watershed land use

209 Hierarchical cluster analysis (HCA) was initially performed on the sampling site dataset,
210 based on the percentage of land use associated with the respective watershed of each studied
211 site (Table 2). The optimal clustering (Figure 2) discriminated five major groups of sites. Group
212 I gathers sites from watersheds dominated by agricultural areas like corn, sunflower and
213 winter or spring wheat. Group II includes sites consist in a combination of forests, agricultural
214 areas and pastures with equivalent surface area percentages (Table 2). Groups III, IV and V
215 represent sites from forest, pasture and vineyard dominated watersheds, respectively.

216 The Group I dominance (23/50 sites) was expected because the Adour-Garonne basin has a
217 large part of field crops (*i.e.* 55%, Figure 2 and Table 2). The Group II (15/50 sites) and Group
218 III (6/50 sites) are consistent because forests represent the second most important part of this
219 territory (*i.e.* 40%). Lastly, there are only three sites in either group IV or V, that was also
220 consistent with overall land use of the basin, with the two main vineyard areas around Cognac
221 and Bordeaux cities, and some small areas of cattle breeding in the medium altitude mountains
222 of Massif Central. Moreover, it would be expected some sites to be locally dominated by
223 artificial territories (*e.g.* Bordeaux and Toulouse metropolises), but in fact, it is never reached
224 high percentages of land use of such watersheds. For each group obtained with the HCA, the
225 inter-group variability was at least 54 % (group IV). This variability, due to the absence of
226 buffer zone determination for each watershed, may lead to some discrepancies between the
227 dominant portion of land use in the watershed and that near the sampled site.

228 3.2. Linking pesticide contamination with watershed land use

229 A principal component analysis (PCA) was performed with the contamination levels
230 measured for the 23 studied pesticides for all periods (n=6) and sites (n=50). This PCA
231 projection (Figure 3 and Figure 4) allowed to visualize local trends in pesticide concentrations
232 and to establish correlations between pesticide contamination patterns and the land use
233 groups defined before (Table 2). Six axes with eigenvalues greater than 1 (Kaiser Criterion)
234 were selected, they explained 73.2 % of the total variance of the dataset. The Varimax-rotated

235 axes loading matrices of pesticides are grouped in Table S 2. The first axis (A1) explained 18.2
236 % of the total variance and had strong loadings (≥ 0.75) related to flurtamone (FTM),
237 epoxyconazol (EPX), cyproconazole (CYP), metolachlor (MTC), and moderate loadings
238 (between 0.50 and 0.75) with tebuconazole (TBZ), atrazine (ATZ) and desethylatrazine (DEA).
239 The second axis (A2) explaining 17.5 % of the total variance had strong loadings with
240 desethylterbuthylazine (DET), desisopropylatrazine (DIA), simazine (SMZ), terbuthylazine
241 (TUZ), and moderate loadings of desethylatrazine (DEA). A two-dimensional plot of A1
242 against A2 (Figure 3) was performed in order to show the correlation between variables and
243 individuals.

244 Figure 3 b allowed the discrimination of two groups (previously obtained with a HCA, Table
245 2 and Figure 2): I and V, which mainly correspond to agricultural areas and vineyards,
246 respectively. The other groups (II, III and IV) were not clearly separated from Group I and did
247 not seem correlated with any of the pesticides having strong or moderate loadings on these
248 first two axes. The first axis structured Group I which includes sites with agricultural areas
249 dominated watersheds (Table 2) and was correlated with CYP, EPX, FTM, and MTC (Figure 3
250 a). The two fungicides (CYP and EPX) and the two herbicides (MTC and FTM) are often used
251 in agricultural context in France, especially for the treatment of cereal, corn and sunflower
252 crops (<https://ephy.anses.fr>). The moderate loadings of TBZ can be explained by the fact that
253 this fungicide is used for both the treatment of cereal crops and vineyards (less specific use
254 than CYP, for example). Then, the moderate loadings of the prohibited ATZ (banned in 2003
255 in France) and its main metabolite DEA illustrate their likely high persistence in soils³⁵⁻³⁷ and
256 recurrent release in waters, since decades after its ban it is still quantified in surface waters¹⁴.
257²⁶. Globally, the correlations between these pesticides and agricultural areas were consistent.

258 A gradient of concentration was observed along A1, with the individuals located on the
259 positive values (Figure 3b). This gradient was explained by the seasonal trends of the
260 contamination levels measured, which are linked to specific treatment periods. In agreement
261 with Bernard, et al.¹⁴, metolachlor concentrations were the highest in May, as the result of the
262 treatment of corn crops at this period (*i.e.* March to June). Group V sites (*i.e.* vineyards
263 dominated watersheds, Table 2) were characterized by SMZ and its metabolite DIA, as well as
264 TUZ and its metabolite DET, along Axis 2. These two pesticides which had been used for the
265 treatment of vineyards are banned since 2003 for SMZ, and 2008 for TUZ. However, they are
266 still quantified in water together with their metabolites¹⁶, as also shown by our data. In a lesser
267 extent, the loading with A2 of norflurazon (NFZ), an herbicide typically used in vineyards

268 during the same period, appears to be consistent in terms of residual contamination. As
269 previously mentioned for atrazine, the presence of these compounds in surface water (and
270 also groundwater) despite their prohibition for several years can be explained by their
271 persistence in soil after their application ³⁸⁻³⁹. For TUZ, a study performed by Carretta, et al. ⁴⁰
272 demonstrated that its dissipation from soil is strongly influenced by the granulometry, organic
273 carbon content and depth. Consequently, quantification of SMZ and TUZ in surface waters
274 can be explained by their remobilization from soil which can depend on soil texture, physico-
275 chemical properties of the compound (including log K_{oc} and log K_{ow} , Table 1), as well as
276 climatic conditions such as rainfall. A study performed by Hildebrandt, et al. ⁵ in three
277 sampling sites of North Spain showed the impact of intensive vineyard cultivation on surface
278 and groundwater quality. In this study, they also demonstrated correlations between these
279 four same pesticides (SMZ, DIA, TUZ and DET) and the presence of vineyards, in agreement
280 with our observations. Complementary information was provided by the other axes. Axis 3
281 (10.8% of the variance) had strong loadings related to chlortoluron (CTU), isoproturon (IPU),
282 and moderate loadings with metazachlor (MTZ) and imidacloprid (IMI) (Table 2), also
283 correlated with group I. This observation is consistent because they are generally all used for
284 the treatment of cereals crops, while Axis 4 (Figure 4) showing moderate loading with
285 dimetomorph (DMM), carbendazim (CBZ) and NFZ correlated with vineyard sites (Group
286 V). NFZ and CBZ were banned in 2004 and 2008, respectively, but as previously mentioned
287 for atrazine they are still quantified in surface waters due to their likely remobilization from
288 the soil ⁴¹. DMM was also quantified in a vineyard watershed by ⁴². Globally, the pesticides
289 correlated with Axis 1 and agricultural areas are mainly herbicides (CTU, IPU and MTZ) as
290 found by Van Metre, et al. ¹⁹, while those correlated with Axis 3 are mainly fungicides (DMM
291 and CBZ). These observations are in agreement with specific pesticides use because vineyards
292 are more sensitive to fungal development than corn crops, for example.

293 To conclude, this PCA revealed that the pesticides quantified in the rivers with POCIS are
294 regularly linked with the main land use of the corresponding watersheds, especially in the
295 case of agricultural areas and vineyards (groups I and V, respectively – Table 2). Conversely,
296 the groups II, III and IV were not clearly associated with the contamination profile found. Such
297 result can be explained by the fact that these sites are assumed either to be slightly or not
298 contaminated by pesticides (*i.e.* areas dominated by forest or pastures), or phytosanitary
299 treatments with various compounds in the case of watershed characterized by mixed land
300 uses. To confirm these statistical analyses and go more in depth in contamination profiles for

301 selected sites identified by the PCA, site fingerprints were further addressed using the waffle
302 method.

303 3.3. Confirmation of statistical observations with pesticide contamination fingerprints

304 The PCA showed that the group III (*i.e.* forests dominated watershed) was not correlated with
305 any peculiar pesticides, suggesting that the corresponding stations are slightly, or even not
306 contaminated. One site among this Group III was chosen in order to illustrate this observation
307 (*i.e.* site n° 5216210, Table 2 and Figure 5 a). For all sampling periods over the year 2016, the
308 pesticide fingerprint of this site showed that it was almost not contaminated by the 23 searched
309 pesticides (Figure 5 b). Only acetochlor (ATC) and alachlor (ALA) were detected in May, but
310 with very low contamination levels, near the QL_P (Table S 1), which can be considered as
311 residual ultra-traces (compounds banned since 2013 and 2008, respectively). The proximity of
312 some agricultural and artificial areas only at the outlet of the watershed does not seem
313 affecting the quality of this watercourse. This observation probably reflects the ability of the
314 river to progressively dilute the pesticides mainly used upstream of the monitoring area.

315 The previous PCA discriminated some sites among the group I (*i.e.* agricultural dominated
316 watershed) according to the axes 1 and 3. The pesticide fingerprints of two sites from the group
317 I with different land use repartition were considered hereafter. For instance, the catchment
318 associated to the site n°5080960 (Figure 6 a) is composed of 81 % of agricultural areas, 15 % of
319 forests and 2 % of pastures and vineyards. Adversely, the watershed of site n°51156950 (Figure
320 7 a) is composed by 82 % of agricultural areas, 12 % of artificial areas (*e.g.* urban areas), 3 % of
321 forest and 2 % of pastures. The pesticide fingerprints (parts b of Figure 6 and Figure 7) can be
322 expected to exhibit high similarities because of agricultural areas dominating within the group
323 I. Nonetheless, some features due to the minor part of their other land use can be noticed, with
324 higher artificial surfaces for the Hers Mort station (Figure 7 a). In these two cases, fingerprints
325 highlighted complex mixtures of pesticides, with the frequent occurrence (≥ 50 % of the 6
326 sampling periods, for a selected chemical) of ALA, ATZ, CTU, FTM, MTC and SMZ as
327 herbicides, or DMM, EPX and TBZ as fungicides. These results showed that the watercourses
328 were contaminated, at least once along the year, by almost all the 23 studied pesticides, in
329 contrast with results obtained previously for a representative site of the Group III (Figure 5 b).
330 In each site, pesticides used specifically in agricultural context were quantified (*e.g.* MTC, TBZ,
331 EPX,...) with varying contamination levels over the year 2016. The month of May provided
332 the highest number of quantified pesticides, with scores of 20/23 and 18/23 pesticides, and
333 the highest contamination levels with average concentrations of $6.44 \mu\text{g L}^{-1}$ and $4.20 \mu\text{g L}^{-1}$ (*i.e.*

334 sums of each quantified contaminant), for the site n°5080960 and the site n°5156950,
335 respectively.

336 These two fingerprints also demonstrated some differences related to the minority land use.
337 Indeed, site n°5156950 (Figure 7) exhibited IMI with high quantification frequency and stable
338 contamination levels, in contrast with site n°5080960 (Figure 6). Until 2016, this insecticide was
339 be used either in agricultural contexts, like cereal crops, or for non-agricultural purposes, like
340 the treatment of private gardens or pets. For site n°5156950, the IMI residual and stable
341 contamination levels can be associated with the non-agricultural context because of the
342 proximity of artificial areas near the sampling site (Figure 7 a)¹⁴. In contrast, IMI contamination
343 of site n°5080960 was rather due to the use of this insecticide in an agricultural context.
344 Actually, it was quantified during Spring and November only, which corresponds to its typical
345 application periods. The same observation can be made for DIU, banned since 2008 in
346 agricultural treatments, which is now used only as a biocide for fouling treatment on house
347 materials, and was observed all through the year at site n°5156950. The site n°5080960 also
348 exhibits some trace levels of residues that were less, or even not quantified on site n°5156950,
349 such as SMZ and NFZ. Such herbicides were characteristic of vineyard treatments in the early
350 2000s in France, and probably correspond here to remnant background contaminations. These
351 results are supported by some vineyards still occurring on the Gupie at Sainte Bazeille station
352 (*i.e.* 2 % of land use, Table 2).

353 This kind of observation is more pronounced with the pesticide fingerprint obtained for group
354 V sites, which were representative of catchments characterized by higher surface of vineyards
355 (Table 2, Figure 8 a). The waffles of the site n°5075900 (Figure 8 b) exhibited a complex mixture
356 of pesticides and metabolites containing NFZ, DMM, SMZ and DIA for each sampling period.
357 But this time, contamination levels were higher than those previously observed for site
358 n°5080960. This observation can be explained by a likely dilution effect occurring at sampling
359 sites located far from the source of contamination (case of site n°5080960)⁴². In addition, TUZ
360 and its degradation product DET were also quantified during all periods⁵, which was not the
361 case for the sites of group I. Conversely, CYP, EPX and FTM were barely or even not quantified
362 on the site n°5075900, which involves their specific uses in vineyard agricultural context. On
363 the other hand, some pesticides typically used on field crops were also quantified on this site,
364 such as MTC, but contamination levels were less marked in this case, with a maximal value of
365 0.5582 µg L⁻¹ (Figure 8 b). TBZ was quantified as well during each period, but with
366 contamination levels closer to agricultural sites of Group I. This observation can be explained

367 by the non-specific uses of this fungicide, as previously mentioned. In addition, other studies
368 performed on either an agricultural ¹⁸ or a vineyard ⁴² watershed quantified this compound.

369 These fingerprints obtained with the waffle method combined with POCIS data confirmed
370 that there is a different and specific pattern to the pesticide impacts of land uses on the surface
371 water quality. These simple graphical representations of TWACs allow seeing quickly which
372 contaminant was mainly quantified and when it occurred. In addition, the waffles allow a
373 quick comparison of the pesticide fingerprints between sites.

374

375

376 4. Conclusions and perspectives

377 The purpose of this paper was to develop and propose a methodology for optimizing the
378 interpretation of the links between land use and pesticides quantified in surface water, using
379 a large dataset. Data used in this study were collected during a 1-year pesticide monitoring
380 performed with the deployment of POCIS during 6 periods of 14 days, over 50 sampling sites.
381 Each site was identified and delimited in function of its watershed, with the associated land-
382 use aggregates. These two datasets were confronted with multivariate analyses such as
383 hierarchical cluster analysis (HCA) and principal component analysis (PCA), which allowed
384 identifying key variables responsible for patterns of sampling sites.

385 The HCA allowed grouping the 50 sites into 5 groups with similar main land uses. The PCA
386 discriminated two groups of sites and showed that some pesticides were specific to a peculiar
387 phytosanitary uses. To confirm these observations, pesticides fingerprints of four sites with
388 opposing land use were compared. These fingerprints confirmed that there is a different and
389 specific pattern related to the pesticide detections with POCIS and the land uses for the
390 concerned catchments. For instance, these fingerprints quickly showed that forest-dominated
391 watersheds display a slight contamination by selected pesticides. In addition, it appears that a
392 minor share of the watershed land use may contribute to the water quality, and some dilution
393 effects would occur when the source was far from the sampling site.

394 However, this methodology could be further improved to demonstrate even finer links
395 between land-use and quantified contaminants with passive samplers. One option would be
396 to apply a buffer of X km around the sampling site or around the linear of the watercourse, in
397 order to reduce the size and spatial variability of the study area ². Another alternative could
398 be to project the graphical land parcel register (RPG -
399 [https://www.data.gouv.fr/fr/datasets/registre-parcellaire-graphique-rpg-contours-des-
400 parcelles-et-ilots-cultureaux-et-leur-groupe-de-cultures-majoritaire/](https://www.data.gouv.fr/fr/datasets/registre-parcellaire-graphique-rpg-contours-des-parcelles-et-ilots-cultureaux-et-leur-groupe-de-cultures-majoritaire/)) in order to identify more
401 precisely the crops near the sampling site, and to achieve a higher level of detail regarding
402 contamination sources.

403 To conclude, this methodology could be considered to establish similar links for other type of
404 contaminants, such as pharmaceutical residues. To do this, the TWACs of these contaminants
405 in the water would be necessary, and then coupled with indicators or characteristic uses on
406 territories.

407

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414 **Conflict of interest**

415 The authors declared no competing interest.

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418

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- 542

543 **Table captions**

544

545 *Table 1. Abbreviations, log K_{ow} (octanol-water partition coefficient), log K_{oc} (organic carbon-water partition*
546 *coefficient), families, biological activities and regulatory status of the 37 studied pesticides; pesticides written in*
547 *bold presented annual quantification frequencies higher than 10%.*

548 *Table 2. The 50 sampling stations with their codes, names, HCA groups obtained, area of the associated watershed*
549 *and land use repartitions.*

550

551

552 **Figure captions**

553

554 *Figure 1. Map projection of the Adour-Garonne basin with the 50 sampling stations selected (black dots); land use*
555 *according to Corine Land Cover 2012; yellow: agricultural areas (i.e. cereal and vegetable crops); orange:*
556 *vineyards; green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major*
557 *river networks.*

558 *Figure 2. Hierarchical cluster diagram of the 50 stations classified based on the percentage of land use; the numbers*
559 *at the bottom of this graphical representation correspond to the station's code (as listed in Table 2); y-axis*
560 *corresponds to the Euclidian distance. The roman numbers in the tree's branches correspond to a posteriori*
561 *established groups stations with dominant land use: I: agricultural areas, II: Combination of forests, agricultural*
562 *areas and pastures; III: forest; IV: pasture; V: vineyard.*

563 *Figure 3. Two-dimensional plot of PCA computed from the concentration of pesticides measured at each sampling*
564 *station and period. The first two axes (A1 and A2) explain 35.7 % of the variability; (a) explanatory variables (23*
565 *studied pesticides identified with their abbreviations, listed in Table 1); (b) individuals (samples) and projection of*
566 *the HCA groups identified with their respective color, the ellipse is drawn around the barycenter of the group,*
567 *darker areas correspond to 50 % of the group's data.*

568 *Figure 4. Two-dimensional plot of PCA computed from the concentration of pesticides measured at each sampling*
569 *station and period. The two axes (A3 and A4) explain 20.2 % of the variability; (a) explanatory variables (23*
570 *studied pesticides identified with their abbreviations, listed in listed in Table 1); (b) individuals (samples) and*
571 *projection of the HCA groups identified with their respective color, the ellipse is drawn around the barycenter of*
572 *the group, darker areas correspond to 50 % of the group's data.*

573 *Figure 5. Station n°5216210 located on the Gave de Pau River at Rieulhes (France). (a) Map projection of the*
574 *watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow:*
575 *agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red:*
576 *artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured*
577 *concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide*
578 *(on the Y-axis, pesticides abbreviation are listed in Table 1); pesticides are grouped by biological activity where*
579 *green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.*

580 Figure 6. Station n°5080960 located on the Gupie River at Sainte Bazeille (France). (a) Map projection of the
581 watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow:
582 agricultural areas (i.e. cereal and vegetable crops); orange: vineyards; green: forests and semi-natural areas; light
583 green: pastures; red: artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles
584 diagrams of measured concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis)
585 and each studied pesticide (on the Y-axis, pesticides abbreviation are listed in Table 1); pesticides are grouped by
586 biological activity where green corresponds to herbicides, red to insecticides, blue to fungicides and purple to
587 metabolites.

588 Figure 7. Station n°5156950 located on the Hers Mort River at Saint Sauveur (France). (a) Map projection of the
589 watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow:
590 agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red:
591 artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured
592 concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide
593 (on the Y-axis, pesticides abbreviation are listed in Table 1); pesticides are grouped by biological activity where
594 green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

595 Figure 8. Station n°5075900 located on the Euille River at Laroque (France). (a) Map projection of the watershed
596 associated with this station (black dot); land use according to Corine Land Cover 2012; orange: vineyards; yellow:
597 agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red:
598 artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured
599 concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide
600 (on the Y-axis, pesticides abbreviation are listed in Table 1); pesticides are grouped by biological activity where
601 green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

602

603 **Supporting information captions**

604 *Table S 1. The 37 studied compounds with their uptake rate values (k_u), sampling rate values (R_s), instrumental*
605 *quantification limit IQL and limits of quantification for POCIS (QL_p) associated with the two analytical*
606 *techniques.*

607 *Table S 2. Varimax rotated axes loading matrices from PCA of pesticide concentrations (n=284); Bold value*
608 *indicate strong loadings (≥ 0.75); Italic value indicate moderate loadings (≥ 0.5 and < 0.75).*

609 *Figure S 1. Data processing applied on the pesticide concentrations obtained after the field deployment of POCIS;*
610 *P: number of studied pesticides; red box: incoming dataset; orange box: outgoing dataset.*

611

612

613

1 *Table 1.*

2

Compound	Abbreviation	Log K _{ow} ^a	Log K _{oc} ^b	Family	Biological activity	Authorized/banned as pesticide (in France, 12/2016) ^{c,d}
Acetochlor	ATC	4.14	2.31	Chloroacetamide	Herbicide	Banned (2013)
Alachlor	ALA	2.97	3.09	Chloroacetamide	Herbicide	Banned (2008)
Atrazine	ATZ	2.50	2	Triazine	Herbicide	Banned (2003)
Azoxystrobin	AZS	2.50	2.63	Strobilurine	Fungicide	Authorized
Carbaryl	CBY	2.36	2.32	Carbamate	Insecticide	Banned (2008)
Carbendazim	CBZ	1.50	2.6	Carbamate	Fungicide	Banned (2008)
Carbofuran	CBF	1.62	1.34	Carbamate	Insecticide	Banned (2008)
Chlortoluron	CTU	2.50	2.15	Urea	Herbicide	Authorized
Cyproconazole	CYP	3.09	2.59	Triazole	Fungicide	Authorized
Desethylatrazine	DEA	1.51	1.26	Triazine	Metabolite	-
Desethylterbuthylazine	DET	2.23	2.17	Triazine	Metabolite	-
Desisopropylatrazine	DIA	1.15	1.84	Triazine	Metabolite	-
1-(3,4-dichlorophenyl)-3-methyl urea	DCPMU	2.94	2.06	Urea	Metabolite	-
1-(3,4-Dichlorophenyl) urea	DCPU	2.65	1.99	Urea	Metabolite	-
Dimetachlore	DMC	2.17	1.8	Chloroacetamide	Herbicide	Authorized
Dimetomorph	DMM	2.68	2.54	Morpholine	Fungicide	Authorized
Diuron	DIU	2.80	3.03	Urea	Herbicide	Banned for agriculture use (2008)/authorized as biocide
Epoxyconazol	EPX	3.30	3.26	Triazole	Fungicide	Authorized
Flurtamone	FTM	3.20	2.52	Furanone	Herbicide	Authorized

Flusilazol	FSZ	3.75	3.22	Triazole	Fungicide	Banned (2008)
Hexazinone	HXZ	1.17	1.73	Triazinone	Herbicide	Banned (2007)
Imidacloprid	IMI	0.57	2.28	Neonicotinoid	Insecticide	Authorized (Banned 2018)
1-(4-isopropylphenyl)-3-methyl urea	IPPMU	2.63	2.17	Urea	Metabolite	-
1-(4-isopropylphenyl) urea	IPPU	2.16	2.25	Urea	Metabolite	-
Isoproturon	IPU	2.50	2.14	Urea	Herbicide	Authorized (Banned 2017)
Linuron	LINU	3.00	2.79	Urea	Herbicide	Authorized
Metazachlor	MTZ	2.49	1.88	Chloroacetamide	Herbicide	Authorized
Methomyl	MTY	1.24	1.4	Carbamate	Insecticide	Banned (2009)
Metolachlor	MTC	3.40	2.3	Chloroacetamide	Herbicide	Authorized
Metoxuron	MTX	1.60	2.08	Urea	Herbicide	Banned (2007)
Norflurazon	NFZ	2.30	2.85	Pyridazinone	Herbicide	Banned (2004)
Norflurazon-desmethyl	NFZD	1.72	3.43	Pyridazinone	Metabolite	-
Pirimicarb	PYC	1.70	2.59	Carbamate	Insecticide	Authorized
Simazine	SMZ	2.18	2.11	Triazine	Herbicide	Banned (2003)
Tebuconazole	TBZ	3.70	3.19	Triazole	Fungicide	Authorized
Terbuthylazine	TUZ	3.40	2.34	Triazole	Herbicide	Banned (2003)
Thiodicarbe	TIC	1.62	2.62	Carbamate	Insecticide	Banned (2008)

3 ^a Data from Ineris (<https://substances.ineris.fr/fr/>)

4 ^b Information from the Pesticide Properties DataBase – PPDB (<http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>)

5 ^c Information from the international office of water (OIEau - <https://dev.oieau.fr/ag-pesticides/substances>)

6 ^d Information from E-Phy-Anses (<https://ephy.anses.fr/>)

7

9 Table 2.
10

Station	Station name	HCA groups	Area of the watershed (km ²)	Artificial surfaces	Agricultural areas	Vineyards	Pastures	Forests and semi-natural areas	Comments
5008000	The Seugne at St-Germain de Lusignan	I	369	2%	76%	8%	2%	13%	
5011600	The Beau at Saint-Médard	I	219	3%	74%	5%	1%	17%	
5012000	The Antenne at Javrezac	I	338	3%	65%	21%	2%	9%	
5013150	The Tourtrat at Reparsac	I	28	3%	64%	24%	0%	8%	
5023100	The Lizonne downstream Bioussac	I	132	0%	67%	0%	7%	26%	
5030000	The Dronne in Coutras	I	5857	2%	57%	0%	6%	34%	
5079100	The Dropt in Loubens	I	2345	1%	74%	5%	6%	13%	
5079200	The Andouille at Roquebrune	I	67	0%	69%	12%	2%	17%	
5080960	The Gupie in Sainte Bazeille	I	219	1%	81%	2%	2%	15%	Agriculture
5083300	The Trec at Longueville	I	334	2%	87%	0%	2%	7%	
5104000	The Garonne upstream Lot	I	71646	3%	52%	1%	9%	33%	
5106850	The Gélise upstream Rimbez	I	338	2%	56%	17%	9%	15%	
5107000	The Grande Baise at Bapaume	I	2523	2%	81%	0%	6%	10%	
5115550	The Gèze at Castelnau Magnoac	I	28	1%	71%	0%	6%	16%	
5129150	The Rieu Tort at Labastide St Pierre	I	132	5%	49%	35%	1%	8%	
5155000	The Save at Grenade	I	2188	2%	81%	0%	8%	10%	
5156950	The Hers Mort at Saint-Sauveur	I	1824	12%	82%	0%	2%	3%	
5157100	The Sausse at Toulouse	I	224	12%	84%	0%	0%	4%	

5158700	The Aussonnelle at Seilh	I	357	21%	60%	0%	1%	18%	
5219000	The Luy at Saint-Pandélon	I	2166	3%	70%	0%	8%	19%	
5228280	The Douze at Mauvezin d'Armagnac	I	604	0%	63%	10%	9%	17%	
5229100	The Midour at Lannemaignan	I	924	1%	65%	7%	11%	16%	
5231370	The Adour at Borderes	I	5857	4%	55%	0%	10%	31%	
5015320	The Eaux-Clares at Puymmerle	II	473	0%	33%	0%	13%	54%	Mix Forests + agriculture + pastures
5042000	The Auvézère at Pont Rognac	II	4885	1%	41%	0%	22%	35%	
5049000	The Vézère at Le Bugue	II	1824	3%	26%	0%	27%	43%	
5054600	The Solane downstream Naves	II	224	6%	33%	0%	31%	31%	
5064000	The Cère at Sansac	II	357	6%	22%	0%	33%	39%	
5068640	The Sumène upstream Valette	II	3831	0%	9%	0%	27%	62%	
5068890	The Rhue at St-Thomas	II	5	1%	6%	0%	40%	52%	
5093550	The Riou Mort downstream Viviez	II	369	7%	28%	0%	32%	33%	
5099170	The Boralde Flaujaguèse downstream Espalion	II	219	0%	3%	0%	45%	52%	
5128000	The Aveyron at Lugans	II	473	2%	29%	0%	34%	35%	
5134000	The Agout at Ambrès	II	4885	3%	36%	0%	17%	44%	
5167008	The Grand Hers upstream Vixiège	II	1850	2%	27%	0%	12%	58%	
5211550	The Luzoué at Monein	II	5	0%	22%	0%	20%	58%	
5225100	The Midouze at Tartas	II	5711	2%	34%	2%	3%	58%	
5226000	The Midouze at Campagne	II	4770	2%	36%	3%	3%	55%	
5065500	The Jordanne upstream Mandailles-St-Julien	III	1850	0%	1%	0%	19%	80%	Forests
5181000	The Garonne at Labarthe Inard	III	3831	3%	11%	0%	8%	78%	
5191000	The Leyre at Lamothe	III	3583	2%	14%	0%	0%	84%	
5191900	The Leyre at Belin Beliet	III	2741	1%	17%	0%	0%	82%	

5216210	The Gave de Pau at Rieulhes	III	2076	2%	3%	0%	7%	87%	
5224100	The Retjons at Tartas	III	257	3%	18%	0%	0%	79%	
5071300	The Mortagne upstream Tauves	IV	2076	1%	6%	0%	84%	10%	
5097000	The Lander downstream St-Flour	IV	604	3%	26%	0%	60%	10%	Pastures
5042085	The Arnac stream at Arnac Pompadour	IV	2188	8%	14%	0%	65%	13%	
5028110	The Barbanne at Libourne	V	924	1%	5%	82%	10%	3%	
5075900	The Euille at Laroque	V	197	2%	10%	62%	4%	22%	Vineyards
5078900	The Vignague at Morizès	V	195	1%	15%	58%	9%	16%	

11

12

Figures

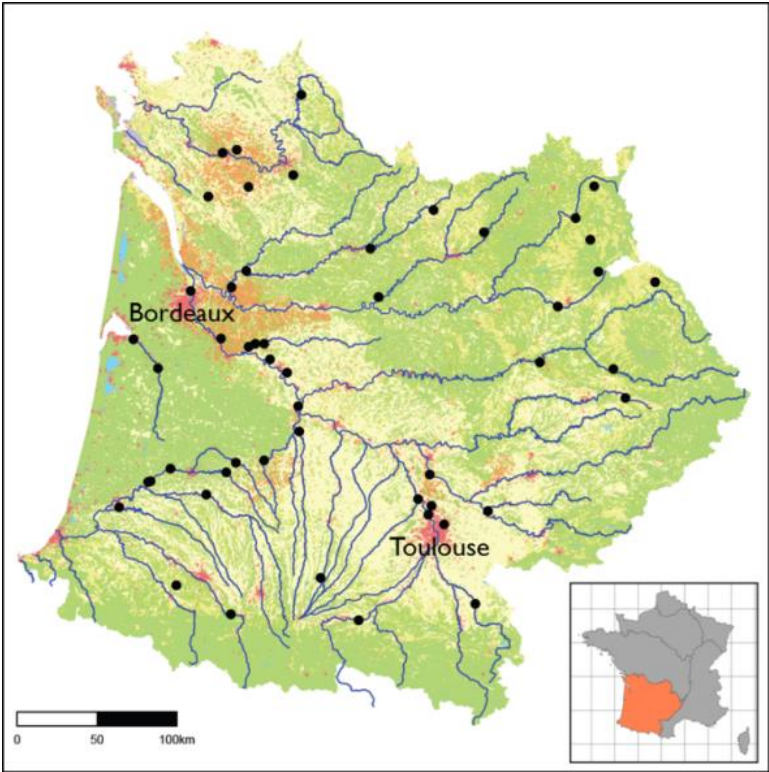


Figure 1. Map projection of the Adour-Garonne basin with the 50 sampling stations selected (black dots); land use according to Corine Land Cover 2012; yellow: agricultural areas (i.e. cereal and vegetable crops); orange: vineyards; green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major river networks.

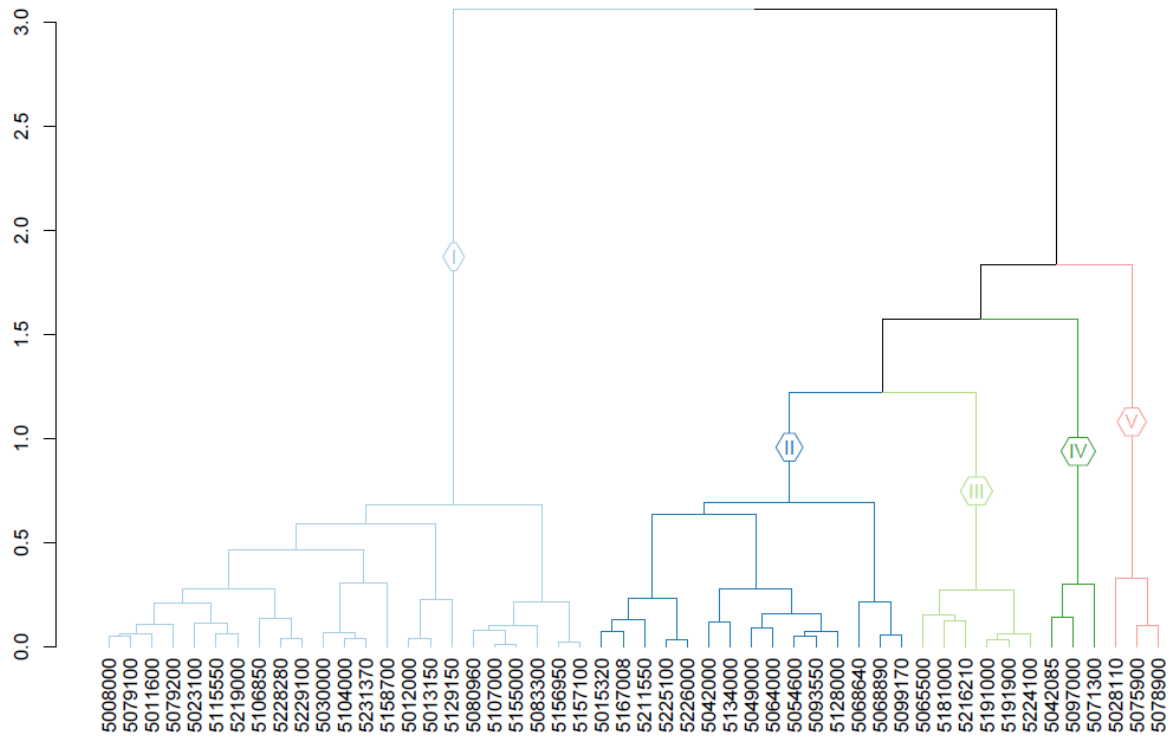
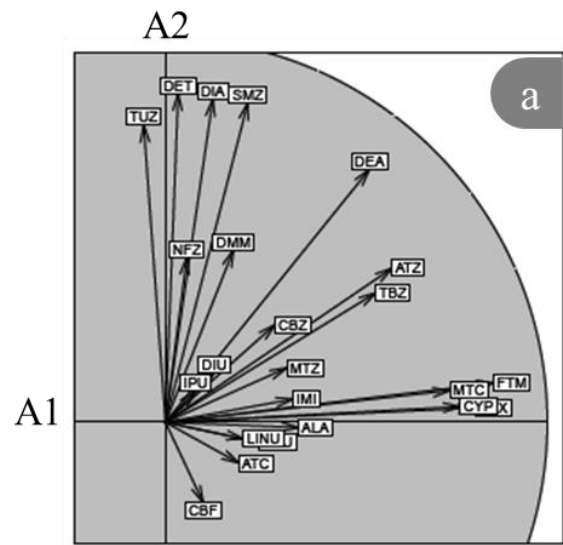


Figure 2. Hierarchical cluster diagram of the 50 stations classified based on the percentage of land use; the numbers at the bottom of this graphical representation correspond to the station's code (as listed in *Erreur ! Source du renvoi introuvable.*); y-axis corresponds to the Euclidian distance. The roman numbers in the tree's branches correspond to a posteriori established groups stations with dominant land use: I: agricultural areas, II: Combination of forests, agricultural areas and pastures; III: forest; IV: pasture; V: vineyard.



○	March
△	May
+	June
■	July
●	September
▲	November

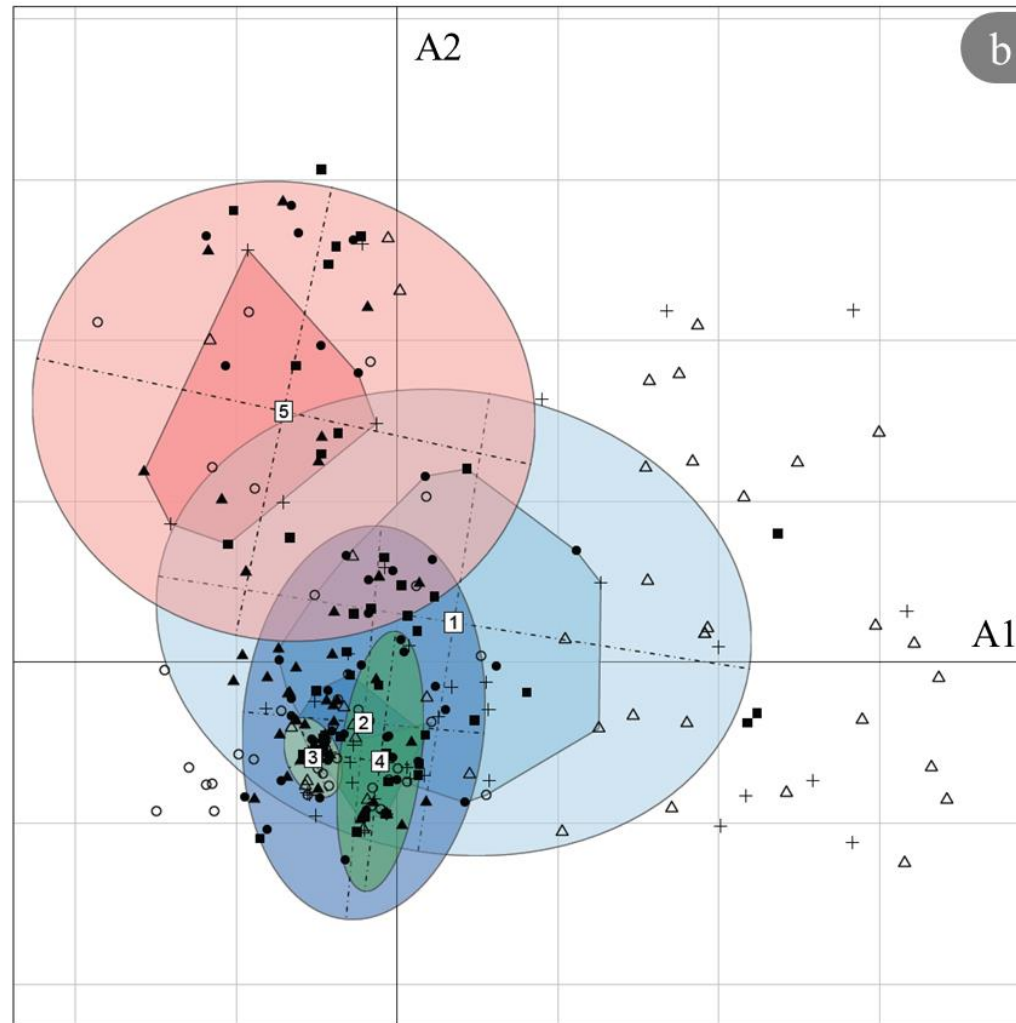


Figure 3. Two-dimensional plot of PCA computed from the concentration of pesticides measured at each sampling station and period. The first two axes (A1 and A2) explain 35.7 % of the variability; (a) explanatory variables (23 studied pesticides identified with their abbreviations, listed in *Erreur ! Source du renvoi introuvable.*); (b) individuals

(samples) and projection of the HCA groups identified with their respective color, the ellipse is drawn around the barycenter of the group, darker areas correspond to 50 % of the group's data.

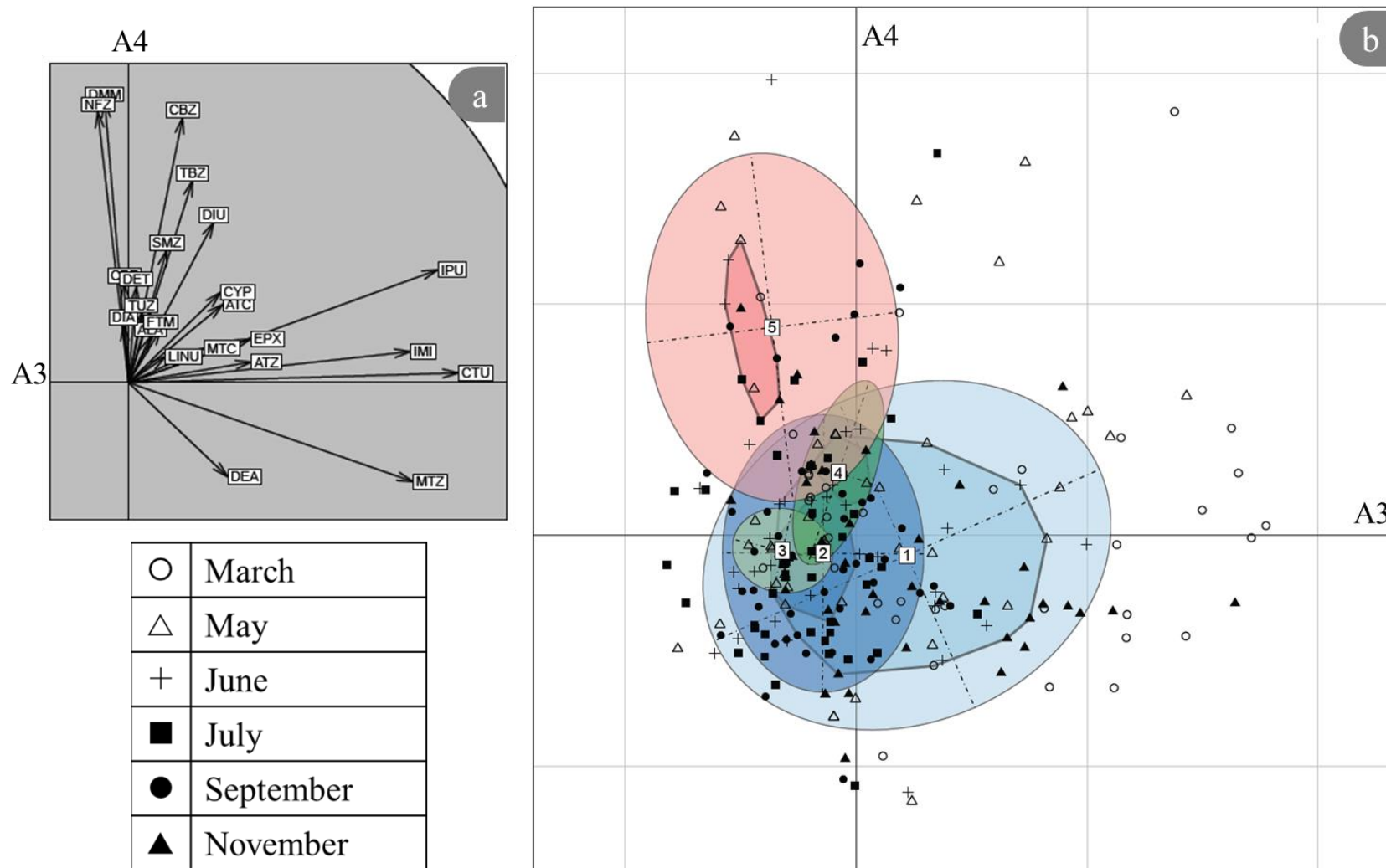


Figure 4. Two-dimensional plot of PCA computed from the concentration of pesticides measured at each sampling station and period. The two axes (A3 and A4) explain 20.2 % of the variability; (a) explanatory variables (23 studied pesticides identified with their abbreviations, listed in *Erreur ! Source du renvoi introuvable.*); (b) individuals

(samples) and projection of the HCA groups identified with their respective color, the ellipse is drawn around the barycenter of the group, darker areas correspond to 50 % of the group's data.

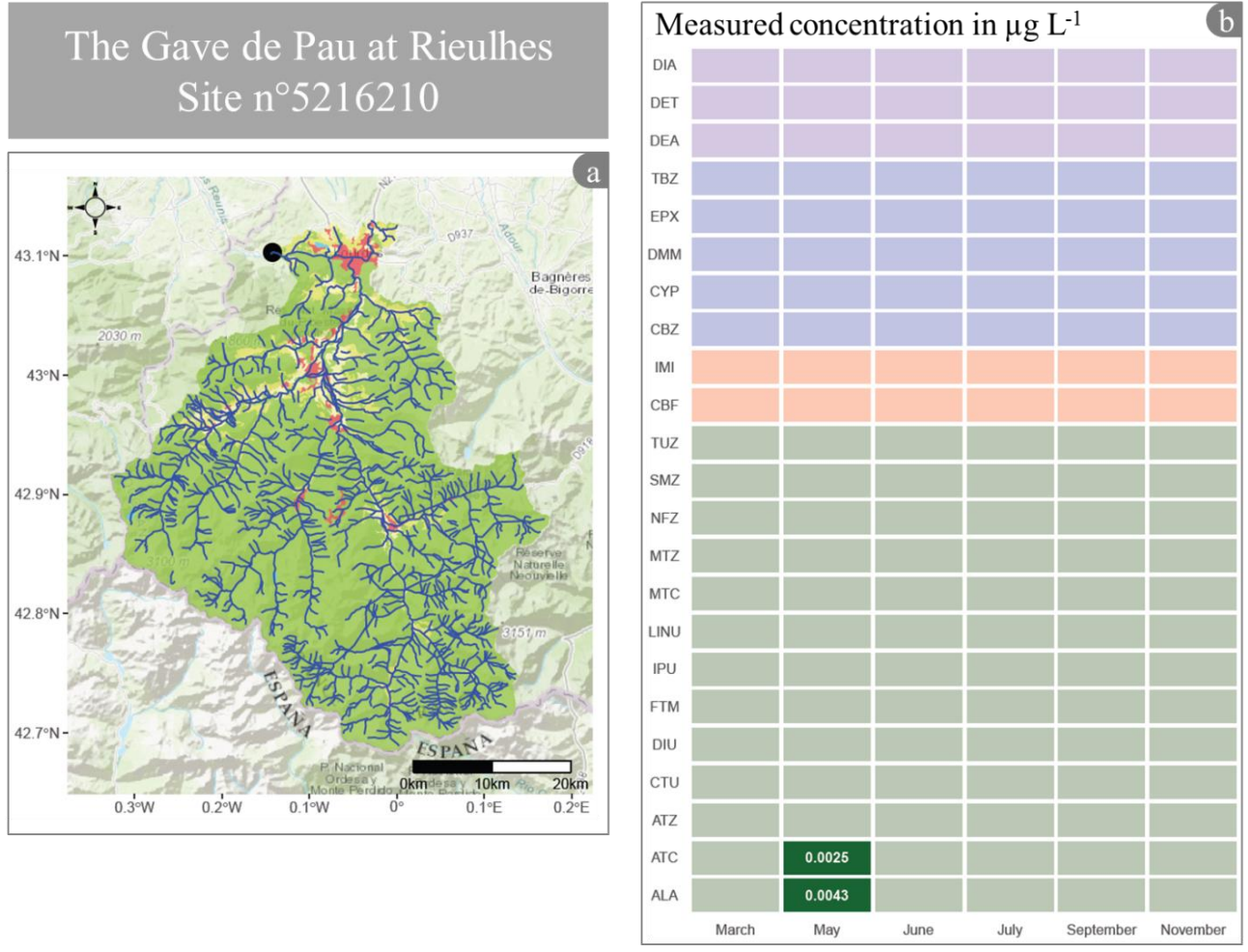


Figure 5. Station n°5216210 located on the Gave de Pau River at Rieulhes (France). (a) Map projection of the watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow: agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide (on the Y-axis, pesticides abbreviation are listed in **Erreur ! Source du renvoi introuvable.**); pesticides are grouped by biological activity where green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

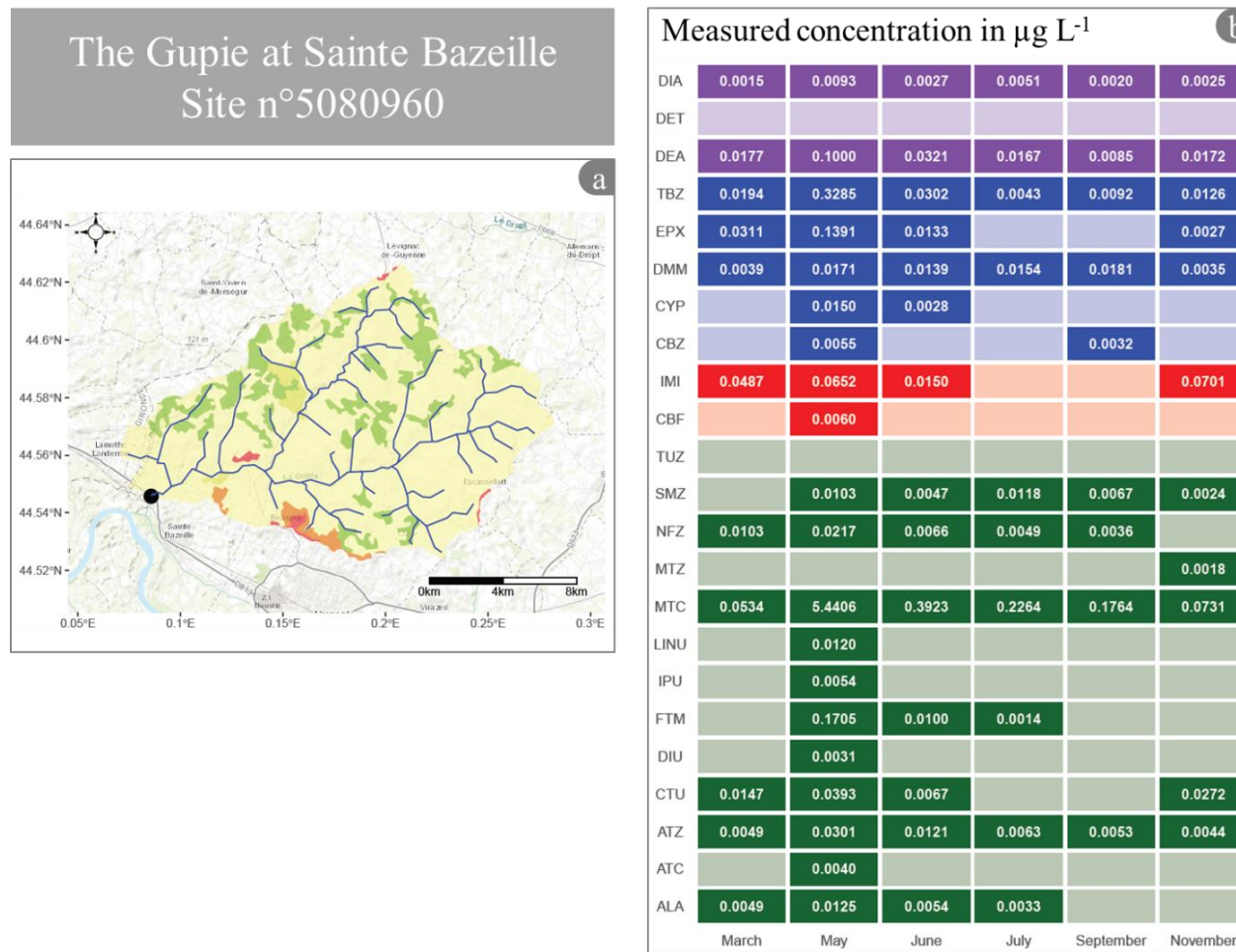
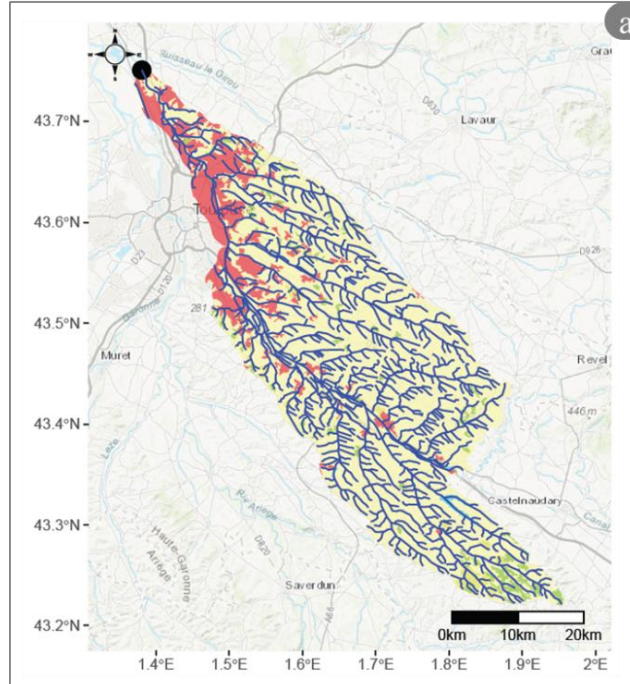


Figure 6. Station n°5080960 located on the Gupie River at Sainte Bazeille (France). (a) Map projection of the watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow: agricultural areas (i.e. cereal and vegetable crops); orange: vineyards; green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide (on the Y-axis, pesticides abbreviation are listed in **Erreur ! Source du renvoi introuvable.**); pesticides are grouped by biological activity where green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

The Hers Mort at Saint Sauveur Site n°5156950



Measured concentration in $\mu\text{g L}^{-1}$

DIA						
DET	0.0017					
DEA	0.0128	0.0287	0.0085	0.0059	0.0043	
TBZ	0.0106	0.3856	0.0348	0.0214	0.0140	
EPX	0.0049	0.1308	0.0187	0.0073	0.0059	
DMM		0.0040	0.0023			
CYP	0.0016	0.0234	0.0012			
CBZ	0.0071	0.0032				
IMI	0.0518	0.0795	0.0306	0.0177	0.0245	
CBF						
TUZ						
SMZ		0.0026	0.0032	0.0015		
NFZ						
MTZ	0.0137	0.0873	0.0077		0.0022	
MTC	0.0603	2.8263	0.4035	0.0787	0.0570	
LINU		0.0670	0.0819	0.1668	0.1363	
IPU	0.0052	0.0061				
FTM		0.1640	0.0039			
DIU	0.0198	0.0889	0.0293	0.0562	0.0159	
CTU	0.2315	0.2746	0.0288	0.0137	0.0107	
ATZ	0.0057	0.0117	0.0040	0.0034	0.0025	
ATC						
ALA		0.0225	0.0035			
	March	May	June	July	September	November

Figure 7. Station n°5156950 located on the Hers Mort River at Saint Sauveur (France). (a) Map projection of the watershed associated with this station (black dot); land use according to Corine Land Cover 2012; yellow: agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide (on the Y-axis, pesticides abbreviation are listed in **Erreur ! Source du renvoi introuvable.**); pesticides are grouped by biological activity where green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

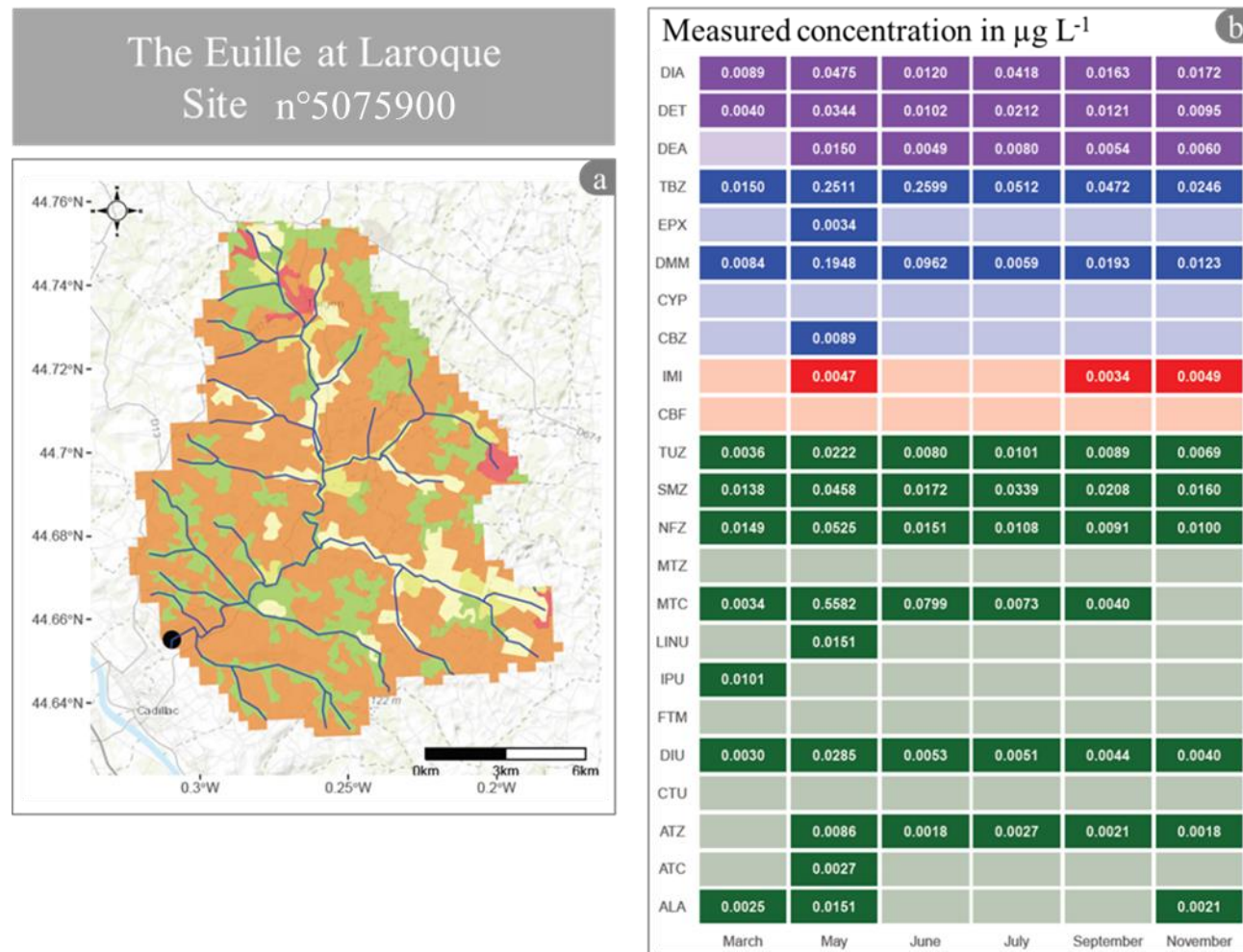


Figure 8. Station n°5075900 located on the Euille River at Laroque (France). (a) Map projection of the watershed associated with this station (black dot); land use according to Corine Land Cover 2012; orange: vineyards; yellow: agricultural areas (i.e. cereal and vegetable crops); green: forests and semi-natural areas; light green: pastures; red: artificial surfaces; blue lines; major river networks. (b) Pesticides fingerprints (waffles diagrams of measured concentration in $\mu\text{g L}^{-1}$) obtained at this station for each sampling period (on the X-axis) and each studied pesticide (on the Y-axis, pesticides abbreviation are listed in *Erreur ! Source du renvoi introuvable.*); pesticides are grouped by biological activity where green corresponds to herbicides, red to insecticides, blue to fungicides and purple to metabolites.

