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1 **Assessing pesticide concentrations and fluxes in the stream of a small**
2 **vineyard catchment - Effect of sampling frequency**

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12 **Abstract**

13 This study reports on the occurrence and behaviour of six pesticides and one metabolite in a
14 small stream draining a vineyard catchment. Base flow and flood events were monitored in
15 order to assess the variability of pesticide concentrations according to the season and to
16 evaluate the role of sampling frequency on the evaluation of fluxes estimates. Results showed
17 that dissolved pesticide concentrations displayed a strong temporal and spatial variability. A
18 large mobilisation of pesticides was observed during floods, with total dissolved pesticide
19 fluxes per event ranging from $5.7 \cdot 10^{-3}$ g/Ha to 0.34 g/Ha. These results highlight the major
20 role of floods in the transport of pesticides in this small stream which contributed to more
21 than 89% of the total load of diuron during August 2007. The evaluation of pesticide loads
22 using different sampling strategies and method calculation, showed that grab sampling largely
23 underestimated pesticide concentrations and fluxes transiting through the stream.
24

25 **Capsule**

26 This work brings new insights about the fluxes of pesticides in surface water of a vineyard
27 catchment, notably during flood events.

28
29
30 **Keywords**

31 Diuron, Flood, Fluxes, Pesticide, Surface water, Vineyard catchment
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33
34

35 **1. Introduction**

36 The intensive use of pesticides for crop protection against diseases led to the widespread
37 presence of these compounds in all the compartments of the environment (soil, water, air).
38 The contamination of surface waters by these biologically active chemicals is an important
39 unwanted side effect of their use. Such contaminations represent a potential risk to aquatic life
40 particularly in rivers draining agricultural areas. Numerous authors have evaluated the
41 transport of pesticides from agricultural lands to rivers (e.g., Clark and Goolsby, 2000; Du
42 Preez et al., 2005; Claver et al., 2006, Blanchoud et al., 2007). Large-scale studies on
43 pesticide losses to surface waters showed that the transfer of pesticides is largely influenced
44 by the intrinsic properties of each compound, but also by the weather conditions, the soil
45 types and land use (Kreuger, 1998; Capel et al., 2001; Riise and al., 2004). The role of
46 hydrology in non point diffuse pesticide pollution is documented, but hardly quantified.
47 Several authors emphasized the significance of rainfall-induced surface runoff as a major
48 source of pesticides in streams (Richards and Baker, 1993; Kuivila and Foe, 1995; Ng and
49 Clegg, 1997; Kreuger, 1998; Capel et al., 2001; Bach et al., 2001; Schulz, 2001a; Schulz,
50 2001b; Holvoet et al., 2007; Vryzas et al., 2009). Rapid flow processes drastically reduce the
51 time available for reactions, such as sorption or degradation, and can lead to a direct transfer
52 of pesticides towards surface waters (Müller et al., 2003). It is widely recognised that during
53 floods, fluxes of many pollutants (e.g., nutrients, metals, pesticides) can vary over several
54 orders of magnitude and may account for the majority of the annual load of pollutants in large
55 river systems (Meybeck, 2005; Zonta et al., 2005; Eyre and Pont, 2003; House and Warwick,
56 1998). Much less is known about pesticide transfer dynamics and loads in small stream
57 systems, where hydrological conditions are subject to fast and considerable variation with
58 time (Gargouma et al., 1997; Ng and Clegg, 1997; Kreuger, 1998; Louchart et al., 2004; Leu
59 et al., 2004; Domange, 2005). Surface waters draining vineyard areas are of specific concern

60 due to the large quantities and diversity of pesticides applied and the vulnerability of
61 cultivated land (i.e., shallow soil depth, steep slopes). Indeed, several studies reported the
62 presence of pesticide residues in surface waters in vineyard areas (Lennartz et al., 1997;
63 Louchart et al., 2001; Ribolzi et al., 2002; Louchart et al., 2004; Rabiet et al., 2008,
64 Hildebrandt and al., 2008). In spite of this highlighted vulnerability of vineyard areas, very
65 few studies reported on the spatio-temporal variability of pesticide concentrations nor on the
66 evaluation of corresponding fluxes. The assessment of pesticide fluxes is essential to evaluate
67 the environmental performance of agricultural practices and to improve water quality at a
68 basin scale. In small stream, Preston et al. (1992) and Cohn (1995) showed that flux estimates
69 of nutrients or metals were often strongly biased when water discharge varied greatly with
70 time.

71 One of the objectives of the European Water Framework Directive (WFD, European
72 Commission, 2000) is to reach a “good status” for European rivers by 2015. The
73 implementation of the WFD implies the intensification of the monitoring of contaminants, the
74 identification of the causes of degradation and the implementation of corrective actions to
75 obtain a good chemical and biological status. For this purpose, Member States have to
76 establish a comprehensive monitoring strategy to establish contaminant exposure levels in
77 surface waters and to evaluate the water quality improvement linked to various management
78 programmes at the catchment scale. Within the WFD, operational monitoring is required for
79 the 33 priority substances; it should be performed via grab sampling 12 times per year.
80 Pesticide transfer during flood events are not specifically considered whereas many studies
81 showed their major role by mobilising great quantity of contaminants. Moreover, several
82 authors (e.g., Schleppe et al., 2006; Johnes, 2007; Horowitz, 2008) have shown for river
83 systems and also small streams that an infrequent monitoring programme, with sampling
84 performed only for a representative range of flow conditions may yield better estimates of

85 solute loads (nutrients, sediment-associated trace elements or major elements) than a routine
86 water quality monitoring programme with sampling at fixed time intervals, regardless of flow
87 conditions The objectives of this work was on the one hand to evaluate the spatiotemporal
88 variability of pesticides concentrations and fluxes in an small-sized vineyard catchment
89 (inferior to 10 km²) and on the other hand to assess the outcome of different sampling
90 strategies on the estimation of pesticide fluxes. In particular, the effect of sampling frequency
91 on the evaluation of pesticide loads and concentrations using several sampling strategies was
92 estimated and discussed.

93 The Morcille catchment was selected for this study as it is a vineyard's area and its small size
94 (8 km²) corresponds to the scale where novel agricultural practices are implemented and
95 evaluated for their environmental performance towards the protection of water quality. One
96 site of the Morcille stream was instrumented in order to monitor both flood and between-
97 flood (base flow) events during one hydrological year. We used various set of monitored data
98 (weekly or monthly grab, weekly automatic fractionated sampling) to compare concentrations
99 and fluxes obtained using these different sampling strategies..

100

101 **2. Material and methods**

102 2.1 Study area

103 The investigation site is the Morcille catchment, which has been studied for a long-time by
104 the Cemagref, french agricultural and environmental engineering research institute. It is a
105 representative catchment of the Beaujolais area for the study of the transport of pesticides
106 from agricultural parcels to surface water (Gouy and Nivon, 2007; Rabiet et al., 2008). The
107 Morcille catchment is located about 70 km north of the city of Lyon in France (Fig. 1). Its
108 small size (8 km²) allows to define a study area where transfers are more easily
109 comprehensible. The head of the basin is essentially covered by forest, whereas downstream it

110 is mainly dedicated to vineyard with the presence of about 70 wine-growers (Gouy and
111 Nivon, 2007). The vine covers about 70% of the catchment's total area (Fig. 2). No industrial
112 activities are present on the site. The hydrology regim of the Morcille stream varies
113 considerably over the year, with instantaneous water flow ranging from 0.005 m³/s (low-water
114 mark) to more than 0.5 m³/s (during storms). It is characterised by significant hydrological
115 events (strong and fast floods). The substratum of the catchment is an altered crystalline
116 basement of mainly granite, with some rather homogeneous soils varying from sandy loam on
117 the upper slopes to more clayey soils in the bottom of the valley (Gouy and Nivon, 2007).
118 Considering the soil texture, the rather steep slopes (varying from 2% to more than 20%) and
119 the presence of a shallow crystalline basement, it is likely that infiltration and sub-surface
120 lateral flow are major processes. Surface runoff only appears during high intensity rainstorms
121 exceeding the soil infiltration capacity. In this area, climatic, geological, topographical and
122 agricultural conditions concur to potentially create very dynamic hydrological conditions and
123 a high erosion rate. Thus, pesticide transfer to surface waters may be favoured. In vineyards,
124 herbicides are applied from the end of March to April, whereas fungicides and insecticides are
125 used from May to August. Considering both hydrologic conditions and pesticide application
126 dates, the more critical period as regards to surface water contamination extends from April to
127 the end of August.

128

129 2.2 Water sampling

130 A monitoring survey was performed from March 2007 to March 2008 during a complete vine
131 growing season. Three sampling sites along the Morcille stream from upstream (1-St-Joseph),
132 intermediate (2-Les Versauds) to downstream (3-St-Ennemon) were monitored in order to
133 approach the spatial variability (Fig. 1 and 2). As for the temporal variability, a sampling
134 strategy was defined so as to investigate the three sites during one year, focusing on the

135 pesticide application periods and the following months. Hence, a more intensive monitoring,
136 with weekly grab samples, was performed from March to September 2007, which included
137 the pesticide application period; a monthly grab monitoring was done thereafter (from
138 October 2007 to March 2008).

139 In order to better identify pesticide concentration amplitude and fluxes during storm events, a
140 specific monitoring was performed at the intermediate site (2- Les Versauds) during spring
141 and summer 2007. Sampling was performed using two refrigerated automated samplers
142 (Bühler, model 4010) with a capacity of 24 polyethylene (PE) bottles. The high capacity of
143 each samplers as well as the use of two samplers allowed to minimize the risk of missing a
144 portion of the flood event. It permitted a fractionated flood sampling at a rate proportional to
145 the flow, allowing to better estimate fluxes than a time dependant sampling. Automatic
146 sampling parameterization was designed using knowledge and experience from the previous
147 two years of flow measurements (2005 and 2006).

148 In addition, in order to compare various sampling strategies to assess pesticide fluxes and
149 mean concentrations in this stream, a weekly composite sampling was performed in July and
150 August 2007 with an additional refrigerated automatic sampler (Bamo, model Aquacell)
151 equipped with a single PE bottle of 10 L. This sampler was also programmed to be
152 proportional to the flow. Thus five sampling methods were compared at site 2: grab sampling
153 (weekly, bi-monthly or monthly), automatic fractionated sampling during storms and
154 automatic weekly composite sampling.

155 In parallel, the water depth was continuously recorded at site 2 with a pressure sensor and
156 converted into water flow values using a sampling-site specific calibration function. Rainfall
157 was measured using two raingauges (i.e. tipping bucket system) located upstream and in the
158 middle of the Morcille catchment (Fig. 2). Data obtained with each gauge were similar and

159 didn't show any significant spatial variability of rainfall. In this study, we reported only the
160 data obtained with the closest rain gauge to site 2.

161

162 2.3 Pesticides analysis

163 Pesticides selection

164 It was not intended to analyse all the pesticides present in surface water of the Morcille
165 stream, but rather to select a range of compounds widely used in vineyard catchment and with
166 various physico-chemical properties. Pesticides were selected among a list resulting from
167 previous screening analysis in surface water at the same site (Gouy and Nivon, 2007, Rabiet
168 et al., 2008). Six pesticides and a main metabolite were chosen from different families of
169 herbicides and fungicides currently used for vineyard treatments: azoxystrobin (AZS),
170 carbendazim (CBZ), dimetomorph (DMM), procymidone (PCM), tebuconazole (TBZ),
171 diuron (DIU) and one of its metabolites: 3-(3,4-dichlorophenyl)-1-methyl urea (DCPMU).
172 Their main physico-chemical properties are presented in Table 1. Diuron, an herbicide largely
173 used on vineyard, is included in the list of the priority substances of the WFD (European
174 Commission, 2000, 2008). Insecticides, although widely used in vineyard to protect crop
175 against pest, were not monitored in this study since occurrence as well as concentrations were
176 found to be negligible in the water bodies of the Morcille watershed (Gouy and Nivon, 2007).

177

178 Chemicals

179 Pure pesticides used for standard solutions or quality controls were of analytical grade and
180 supplied by Cluzeau Info Labo (Sainte Foy la Grande, France) or Sigma Aldrich (Saint
181 Quentin Fallavier, France). Organic solvents used were pesticide or HPLC grade (SDS,
182 Peypin, France).

183 The individual stock solutions were prepared in acetone at a concentration of 100 mg/L and
184 stored at 4°C. These stock solutions were stable for 2 months. Standard working solutions at
185 various concentrations were prepared weekly by appropriate dilutions of the stock solutions in
186 ultrapure water/ acetonitrile (80/20, V/V).

187

188 Sample pre-treatment

189 Except for weekly composite sampling, samples were collected within a maximum of 24 h
190 after sampling and returned to the laboratory for immediate filtration. Water samples were
191 filtered on glass fiber filters (0.7 µm, Ø=47 mm, GF-F Whatman, Sodipro, Echirolles,
192 France). Extraction was carried out on solid phase extraction (SPE) cartridges (Oasis HLB, 60
193 mg, 3 mL, Waters, France) after spiking with linuron used as analytical control standard. Ten
194 µL of internal standard control (deuterated diuron) were added to the final extract of 240 µL
195 water/acetonitrile (80/20, V/V). The concentration factor was about 1000. The organic
196 extracts and corresponding calibration standards were kept at -20°C prior to analysis.

197

198 Analysis

199 Water sample extracts were quantified by ESI-LC-MSMS (LC 1100 Agilent, API 4000
200 Applied Biosystems, Courtaboeuf, France). The compounds were separated on a 250×2 mm
201 Purospher Star RP-18 column (Merck). The mobile phase was water/acetonitrile gradient at
202 0.3 mL/min. The limit of quantification (LQ) ranged between 0.020 and 0.080 µg/L according
203 to the pesticides, and recoveries varied from 80 to 107%, depending on the concentration
204 level and the compound (Margoum et al., 2007). All the concentration results presented in this
205 study were then corrected with the corresponding recovery rate.

206

207

208 2.4. Quality assurance

209 Possible losses of compounds by sorption or degradation during sample collection, storage
210 and transport was evaluated in two separate laboratory studies. First, pesticide stability during
211 storage in PE bottles was assessed. Mineral Evian water (3 replicates) was spiked with the
212 studied pesticides (5 µg/L) and then stored in the same conditions as during monitoring (at
213 4°C in darkness). Pesticides analyses were performed at time 0, 1 h, 24 h, 48 h and 7 days in
214 order to simulate different time of storage inside the automatic samplers. Results are
215 presented in Figure 3. Diuron is the most stable compound in PE bottle with losses below 3%,
216 even over a seven days period. For dimetomorph and DCPMU, losses are below 10% during
217 storage. It is also the case for procymidone over a 2 days period. However, over a seven days
218 period, procymidone showed a significant decrease of concentration, with about 40% of
219 losses. This behaviour could be due to its relatively high K_{oc} (Table 1). Despite their
220 respectively low half life and high K_{oc}, azoxystrobin and tebuconazol showed a good
221 stability, with maximum losses reaching a maximum of 15% over 7 days. In conclusion,
222 stability of all compounds is satisfying over 7 days, except for procymidone; thus average
223 weekly concentrations of procymidone might be somewhat underestimated.

224 In the second study, spiked and unspiked mineral water (Evian) were run through the
225 automatic sampler (i.e., passing through the tubes and collected in the receiving bottles of the
226 sampling equipment) in order to verify the potential loss of pesticides and the absence of
227 contamination, respectively. No significant adsorption or release of pesticides was observed
228 (i.e., the relative difference of pesticide concentrations before and after the sampler was
229 below 5%).

230 Field and analytical blanks (using ultrapure water in PE bottles) were also performed for each
231 monitoring campaign.

232

233 2.5. Flux calculation

234 Pesticide fluxes were estimated at site 2 over various periods and using different data and
235 calculation methods.

236 The weekly load of pesticides (WL) was calculated for the March-September period, using
237 the manual weekly sampling data, by multiplying the average weekly stream flow by the total
238 pesticide concentration (i.e., sum of the concentrations of the 8 studied pesticides) measured
239 on grab samples as follows:

$$240 \text{ WL } (\mu\text{g}) = Q \times C_i \times t_i \quad \text{equation (1)}$$

241 where Q is the average weekly stream flow during the considered period t_i (L/s); C_i is the
242 concentration of total pesticides analysed in grab samples collected once a week ($\mu\text{g/L}$); and t_i
243 is the considered time period (s) (seven days surrounding the sampling day).

244 For the monthly monitoring, over the October-March period, monthly pesticide fluxes were
245 estimated in the same way by multiplying the average monthly stream flow by the total
246 pesticide concentration measured on the samples collected manually once a month.
247 Concentrations below the LQ were set to half of the LQ for these calculation. Compounds not
248 detected were set to 0.

249 The total pesticide load during a flood (FL) was calculated using the following equation:

$$250 \text{ FL } (\mu\text{g}) = \sum q_i \times \overline{C}_i \times t_i \quad \text{equation (2)}$$

251 with q_i , the instant flow at the time i (L/s); \overline{C}_i , the concentration value linearly interpolated
252 between both nearest measured pesticide concentrations ($\mu\text{g/L}$); and t_i , the time interval
253 between the flow measurements (s). This time varied from several seconds to minutes.

254

255

256

257

258 **3. Results and discussion**

259

260 **3.1 Hydrological context**

261 Daily rainfall (mm) and water flow (L/s) of the Morcille stream at site 2 for the study period
262 (from 01/03/2007 to 31/03/2008) are presented in Figure 4. Total annual precipitation during
263 year 2007 was about 909 mm. This value is not significantly different from the average
264 annual precipitation during the past fifteen years (860 mm). However, summer was
265 particularly wet in 2007, with a total precipitation of 426 mm from May to August (Fig. 4),
266 compared to 290 mm in average (for the past fifteen years) (Meteo France). Especially, the
267 months of June and August were particularly wet (125 and 101 mm respectively, versus an
268 average of 67 and 78 mm, respectively). This specific context could contribute to increase
269 surface water contamination by pesticide: on the one hand, a higher occurrence of storms in
270 summer is favorable to surface runoff contributing to mobilise more pesticides, and, on the
271 other hand, wet conditions often lead farmers to use more pesticides than a normal year,
272 because of a higher risk of crop disease.

273

274 **3.2. Grab monitoring of pesticide concentrations along the Morcille stream**

275 Dissolved herbicides and fungicides concentrations measured from grab weekly and monthly
276 samples along the Morcille stream from 6 March 2007 to 18 March 2008 are reported in
277 Figure 5.

278 The presence of pesticides was demonstrated throughout the investigation period with a large
279 seasonal variation, corresponding to the pesticide application calendar. Indeed, total pesticide
280 concentrations range from below the LQ to 16.4 µg/L. Diuron and DCPMU concentrations
281 ranged from below the limit of quantification (LQ) to 13.3 µg/L (Fig. 5a). Concentrations
282 were below 0.2 µg/L in March 2007 and 2008, corresponding to a residual background linked
283 to previous vineyard treatments. DIU and DCPMU concentrations increased in the stream at

284 the beginning of April 2007, according to the onset of herbicide spreading on vineyard. The
285 highest herbicide concentration was observed in May and June and at the beginning of July.
286 Total fungicide concentrations were very low in March and April 2007 (below 0.3 µg/L). In
287 May, fungicide concentrations increased slightly with values ranging between 0.3 and 0.9
288 µg/L at the downstream site. Starting in June, fungicide concentrations rose sharply. The
289 maximum concentration was observed in July with 8.3 µg/L at site 3 (Fig. 5b).
290 Herbicide as well as fungicide concentrations decreased in August, but remained at a
291 detectable level during all year round: this was especially the case for diuron, mainly applied
292 in late winter but also locally until early summer due to the wet conditions. Thus, surface
293 water contamination by pesticides largely overstepped the application period, as shown by the
294 high pesticide concentrations still present in January (up to 2.0 µg/L at site 3).
295 Besides seasonal variations, we observed a large variability of pesticide concentrations with
296 time, over very short periods. For instance, between the 30 May 2007 and the 05 June 2007,
297 diuron and metabolite concentrations at site 3 increase from 0.3 to 13.3 µg/L. This high
298 reactivity may be related to the rapid pesticide transfer via runoff due to storm events, which
299 can mobilise a large and variable quantity of pesticides. Indeed, this period of the year was
300 marked by large rainfall, with about 55 mm during one week (cf. Fig. 4); this led to a shorter
301 delay between pesticide application and precipitation and favouring the direct transfer to
302 surface water.
303 We present in Figure 6 the relationship observed between total dissolved pesticide
304 concentrations and water flow during grab monitoring at site 2. The positive linear regression
305 is statistically significant ($r^2= 0.78$; $P<0.0001$). The low pesticide concentration for high flux
306 corresponds to a sample collected during a storm event at the end of summer, thus at the end
307 of the application period.

308 We noted that pesticide concentrations generally increased with water flow during the
309 application period and the following months as well, when it is likely that pesticide input to
310 soil and their availability in soil is still significant. This underlined the major role of
311 hydrological conditions on the mobilisation of pollutant. As for pesticide occurrence during
312 base flow, it is assumed that it can be related to the slow processes of water movement
313 through the soil matrix such as subsurface runoff, drainage and exchanges with shallow water
314 table (Müller et al., 2003).

315 On a spatial point of view, we measured a large increase of pesticide concentrations from
316 upstream to downstream, which is coherent with the increasing proportion of vineyard surface
317 downstream (Fig. 2). Indeed, at the upstream reference site (site 1), only diuron and its
318 metabolite, as well as dimetomorph and procymidone were quantified and only twice at low
319 levels (from the LQ up to 2 µg/L). This reflects the small impact of vineyard treatment at the
320 upstream site, whereas at the outlet, pesticides were systematically quantified with a mean
321 concentration of total pesticides of 3.2 ± 4.0 µg/L at site 3.

322 The distribution between the different compounds/molecules at site 2 is reported in Figure 7.
323 Diuron predominated, with concentrations ranging from 0.01 µg/L to 7.5 µg/L. Thus, the
324 average concentration of diuron (1.2 ± 2.0 µg/L) largely exceeded the European
325 environmental quality standard (EQS) of 0.2 µg/L expressed as annual average value
326 (European Commission, 2008). Moreover, at site 3, the downstream site, more than one third
327 of the samples exhibited diuron concentrations higher than the maximum allowable
328 concentration (MAC) of 1.8 µg/L (European Commission, 2008). These results reflect the
329 strong impact of diuron used in vineyard on the surface water quality all along the year.
330 Moreover, DCPMU, a main metabolite of diuron, was systematically quantified with
331 concentrations ranging between 0.01 and 0.5 µg/L at site 2. At site 3, DCPMU concentration
332 ranged between 0.2 and 1.4 µg/L, with a mean concentration of 0.3 ± 0.3 µg/L. Dimetomorph

333 and procymidone, two fungicides commonly utilized on vines, were mostly quantified during
334 the month of July, with concentrations reaching up to 3.4 and 1.3 $\mu\text{g/L}$ respectively at the
335 intermediate site, reflecting their application period on the basin. Tebuconazol was detected
336 all along the application period at site 2 with concentration ranging between 0.02 and 1.9
337 $\mu\text{g/L}$, corresponding to an average concentration of $0.2 \pm 0.3 \mu\text{g/L}$. Carbendazim and
338 azoxystrobin were less often quantified in the stream, with mean concentrations of 0.1 ± 0.2
339 $\mu\text{g/L}$ and $0.08 \pm 0.09 \mu\text{g/L}$, respectively at the downstream site (site 3).

340 The weekly load of total dissolved pesticides at site 2, estimated from equation (1), ranged
341 between 3.3 g and 337 g over the study period. This lead to an annual load of pesticides of
342 2200 g then 12.5 g/Ha taking into account the vine surface drained at site 2 (175 Ha). More
343 than 50% of this amount (1088 g) was transferred during June and July only, with 623 and
344 465 g, respectively. Noteworthy, diuron and its metabolite represented 68% (1502 g) of the
345 annual total load. It represented about 8.6 g of diuron and metabolite per hectare. Considering
346 the recommended amount of diuron to be applied per hectare and per year on this type of
347 culture (i.e., 1500g/Ha, Couteux and Lejeune, 2007), about 0.57% of the total amount of
348 applied diuron reached the Morcille stream. Noteworthy, the load of exported diuron should
349 probably decrease in the future, as its use is no longer authorized. This value is in agreement
350 with measured pesticide losses to surface water reported by other authors (for cereal cultures),
351 ranging from 0.01 to 0.5% of application amounts (Brown et al., 1995; Kreuger, 1998). In
352 fact, our calculation was based on pesticide concentrations measured in weekly grab samples,
353 which mainly corresponded to base-flow conditions; thus it did not take into account the
354 majority of high-flow events, likely to contribute to annual pesticide load transiting through
355 the Morcille stream. We might consider that the estimation of 0.57% of diuron losses
356 probably largely underestimates the actual quantity of diuron exported from vine parcels to
357 the stream. However, in a Mediterranean vineyard catchment, Louchart et al. (2001)

358 estimated to 0.52% the total seasonal losses for diuron, including losses by storm flow and
359 baseflow. This lower value compared to our result is probably due to different characteristics
360 of the watershed studied, in particular the slope; alternatively it might result from differences
361 in the monitoring and calculation methods. In this study, base flow only contributed to 4% of
362 total losses.

363

364 3.3. Storm events monitoring during spring and summer 2007

365 We monitored 8 floods from April to September 2007. Among them, 5 floods were fully
366 monitored and 3 floods could only be sampled in the region of the water flow peak. Sampled
367 flood events were characterised by a maximum water flow ranging between 0.03 and 0.78
368 m³/s and a duration lasting between 2 and 11 hours. These characteristics are typical of most
369 events taking place in the Morcille catchment (Taillandier, 2008).

370 The maximum pesticide concentration recorded during each flood event, as well as the total
371 flux are presented in Table 3 for each monitored compound. Figure 8 presents the distribution
372 of diuron concentrations during the 8 monitored floods, as it is the main pesticide quantified
373 during the study period.

374 As expected, we observe a large mobilisation of diuron in the stream during the high flow
375 events. Concentrations rose rapidly, then usually hit the highest point almost at the same time
376 as water flow peak (Fig. 8). However, a lag time (ranging between few minutes and more than
377 1 hour according to the event) was sometimes observed before or after the maximal pesticide
378 concentration, in comparison with the water flow peak. Concentrations declined thereafter.
379 Maximum pesticide concentration during the 8 monitored floods ranged from 4.8 µg/L (27
380 September 2007, outside the spreading period) to 140 µg/L (01-02 July 2007, considered as
381 exceptional) with an average value of 26.7 ± 42.8 µg/L. The 01-02 July storm event was
382 characterized by very high concentrations of all monitored pesticides (about 10 times higher

383 than for other flood events). Thus, we considered this event as exceptional, probably due to
384 the occurrence of the flood just after pesticides application.. Some authors (Louchart et al.,
385 2001; Leu et al., 2004; Phillips and Bode, 2004) have indeed shown that the major pesticide
386 losses occurred during the first rain event after application. Excluding this exceptional event,
387 as well as the event taking place out of spreading period (end of September), maximum
388 concentrations during floods were between 7.3 and 21.1 $\mu\text{g/L}$, with an average value of 12.7
389 $\pm 4.3 \mu\text{g/L}$. Among all the monitored pesticides, diuron was the most mobilised compound
390 during flood. Its contribution reached up to 76% of the total pesticide load transiting during
391 flood. Maximum diuron concentrations observed during the flood events were always higher
392 than the MAC (European Commission, 2008).

393 Depending on the flood (and excluding the extreme event of 01-02 July 2007), pesticide
394 maximum pesticide concentrations varied by a factor of 3 only, whereas peak water flows
395 varied by a factor of up to 30. Thus, maximum pesticide concentrations did not seem to be a
396 simple function of water flow and it is likely that other processes interfered, such as pesticide
397 availability via runoff.

398 During floods, the total dissolved pesticide fluxes ranged from 1.0 to 60 g. When occurring
399 immediately after application, even a flood of moderate intensity could in fact deliver to the
400 stream a significant load of pesticides in a very short period.

401

402 3.4. Significance of the sampling strategy on the estimation of diuron fluxes and
403 average concentration

404 Flux estimation

405 In order to assess the effect of the sampling strategy on the estimation of diuron fluxes and
406 average concentration, we used different methods and various set of data monitored at site 2
407 in August 2007. This specific month was chosen for this exercise since a majority of the

408 storm events during this period could be collected (Fig. 9). Besides, pesticide concentrations
409 during this period were still very significant.

410 The monthly diuron flux was estimated using weekly, bimonthly or monthly simulated grab
411 monitoring by choosing either the first, second, third or fourth weekly sample as the reference
412 concentration for the calculation; or alternatively, by using only 1, 2 or 4 weekly data. In
413 addition, diuron monthly flux was calculated using the weekly average composite sample
414 concentrations. Finally, diuron monthly flux was estimated for either base flow only, using
415 grab samples collected during base flow conditions; or storm flow conditions only, using
416 automated sampling performed during floods. For the floods that could not be monitored
417 during this period, we estimated the corresponding diuron fluxes using an empiric linear
418 model derived from observed data. Indeed, excluding the extreme event of 01-02 July 2007, a
419 linear regression ($r^2=0.91$) was obtained between diuron fluxes during flood events and the
420 total volume of water conveyed during the event. Thus, diuron flux during a flood could be
421 estimated with the following equation:

$$422 \quad \text{Diuron flux (g)} = [\text{Water volume (m}^3) \times 3.6 \cdot 10^{-3}] - 0.1 \quad \text{equation (3)}$$

423 Although only 7 data points were available to derive this relationship (cf. Fig. 10), it allowed
424 to estimate with less than 30% of bias diuron load during a flood event taking place during the
425 considered period (Table 4). Due to pesticide decay with time and to the limited range of
426 water flow values used to build this equation, the validity of this equation is clearly limited to
427 the study period and it would be incorrect to use it in another context and purpose.

428 Results are presented in Figure 11. According to the method used, diuron monthly fluxes
429 ranged from 4.7 to 73.9 g. The highest value corresponded to the calculation using the weekly
430 composite sampling results, which was considered as the most accurate evaluation. Hence,
431 this value was used thereafter to estimate the bias due to grab sampling. Monthly diuron
432 fluxes, estimated from grab monitoring (weekly, bimonthly or monthly) varied between 4.7

433 and 41.2 g, which is significantly lower than the “most realistic” flux value (73.9 g). Even the
434 grab weekly surveys underestimated pesticide flux by a factor of about 5 at most. As a matter
435 of fact, in August 2007 around 89% of the diuron load were transported during floods, which
436 in total lasted for less than 5 days (i.e., 15% of the time). These results are similar to those of
437 Chen et al. (2005) and Louchart et al. (2001) showing that floods contributed to 90% and 84%
438 (at the field scale) respectively, of the total load (for flood season and annual time scale
439 respectively) of pesticides. This observation shows the major role of storm events in the
440 mobilisation of pesticides. Pesticide losses during baseflow appeared to be of minor
441 importance in comparison with losses during storm flow. A grab monitoring could take into
442 account only partially at best the rapid pesticide transfers. Thus, it results in non-
443 representative average concentrations and loads, and in a higher probability of mis-
444 interpretation of the water quality status, as showed as well by Holvoet et al. (2007). A
445 combined monitoring survey during base flow and storm flow allowed to evaluate the
446 temporal variability in pesticide concentrations. Moreover, the total diuron flux could be
447 derived with a good precision: indeed our estimation reached 53.6 g, that is 72.5% of the
448 “reference” value (Fig. 11). However, it corresponded to a high technical, material and
449 analytical cost investment.

450

451 Estimation of annual average and monthly average diuron concentration

452 The annual average diuron concentration ranged between 1.2 ± 2.0 µg/L using weekly
453 monitoring (4 samples per month during the application period, then one sample per month,
454 that is n=35 samples), and 1.4 to 1.6 ± 2.5 µg/L with monthly monitoring (n=12) (Table 3).
455 Thus, both sampling methods lead to comparable average and standard deviation results, as
456 previously showed for flux estimates. Moreover, monthly average diuron concentrations were
457 calculated for August, using the data obtained through the different monitoring strategies

458 (grab and automatic weekly composite samples). Results showed that average diuron
459 concentration ranged from $0.4 \pm 0.4 \mu\text{g/L}$ using weekly grab sampling data ($n=4$) to 1.6 ± 1.2
460 $\mu\text{g/L}$ using average composite sampling ($n=4$). Combining monitoring during base flow and
461 storm flow, (using the estimated diuron flux, 53.6 g, cf. Fig. 11, and total water volumes
462 conveyed during the month, 42300 m^3) lead to an average diuron concentration of $1.3 \mu\text{g/L}$ in
463 August, in good agreement with the average concentration obtained using the composite
464 weekly sampling. Obviously, grab monitoring, even at a weekly rate, underestimated the
465 average concentration in the Morcille stream.

466

467 **4. Conclusion**

468 The present study reported the great spatial and temporal variability of some herbicide and
469 fungicide concentrations monitored during one year in an agricultural catchment devoted to
470 vineyard. Their occurrence was closely related to the application calendar and the
471 hydrological conditions. Pesticide concentrations were higher during the application season,
472 with maximum concentrations occurring during June and July. Concentrations largely
473 exceeded water quality criteria for the protection of aquatic life. Pesticides were measured in
474 surface water for several months after the application and in the case of diuron, throughout
475 the year. It pointed out their potential to persist in soils and shallow groundwater. The loss of
476 diuron in the catchment outflow was evaluated at 0.57% of the applied amount, which is in
477 agreement with literature data. However, as shown by our study on the effect of sampling
478 strategy, this value is certainly largely underestimated due to grab sampling. Our study of
479 pesticide behaviour during floods showed the major role of hydrological conditions in the
480 transport of pesticides. Indeed, floods contributed to more than 89% of the total load of diuron
481 transiting through the stream during August 2007. These results provided further evidence
482 that floods are the dominant pathways for the transport of pesticides in a small agricultural

483 stream characterized by shallow soils and preponderant surface flow pathways. Using
484 comprehensive data obtained in August, we showed that the estimated diuron fluxes and
485 average concentrations were comparable using either weekly composite sampling
486 (proportional to the flow), or with a combined grab sampling during base flow and automated
487 sampling during floods.

488 A major conclusion of this study was that grab monitoring of surface water is not adapted for
489 an accurate assessment of the contaminant exposure level, especially in dynamic hydro-
490 systems such as the Morcille stream, where it largely underestimates the pesticides
491 concentration and fluxes. These observations have important consequences for the monitoring
492 requirements of pesticides, in the view of the implementation of the WFD.

493

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500

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623

624 **Figures captions**

625 Figure 1. Location of the Morcille watershed and the sampling sites.

626 Figure 2. Land use at the three sampling sites on the Morcille watershed.

627 Figure 3. Study of pesticide stability during storage in PE bottles over a seven days period. Y-
628 axis is the ratio expressed in percent of the concentration of pesticide at time t (C) over the
629 concentration at t0 (C0).

630 Figure 4. Daily rainfall (mm) and water flow (L/s) at site 2 in the Morcille catchment from
631 March 2007 to March 2008.

632 Figure 5. Pesticides concentrations (in $\mu\text{g/L}$) along the Morcilles stream from March 2007 to
633 March 2008; a: Diuron and DCPMU; b: Total fungicide (sum of the five fungicides
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635 Figure 6. Water flow (m^3/s) versus total pesticide concentrations ($\mu\text{g/L}$) in the Morcille stream
636 at site 2 during weekly monitoring (March 2007 to September 2007).

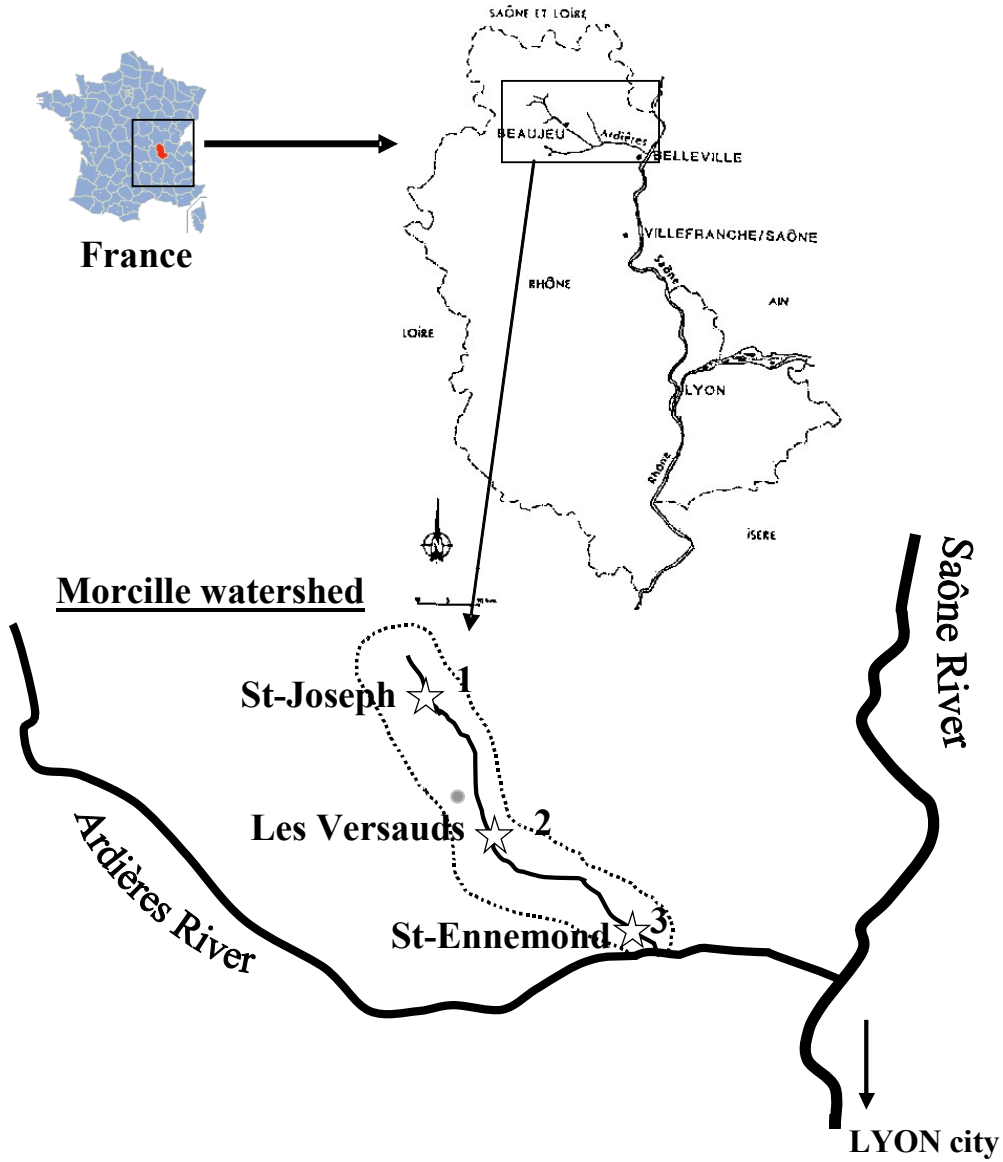
637 Figure 7. Dissolved pesticide concentrations ($\mu\text{g/L}$) at site 2 from March 2007 to March 2008.

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645 methods and monitoring data.



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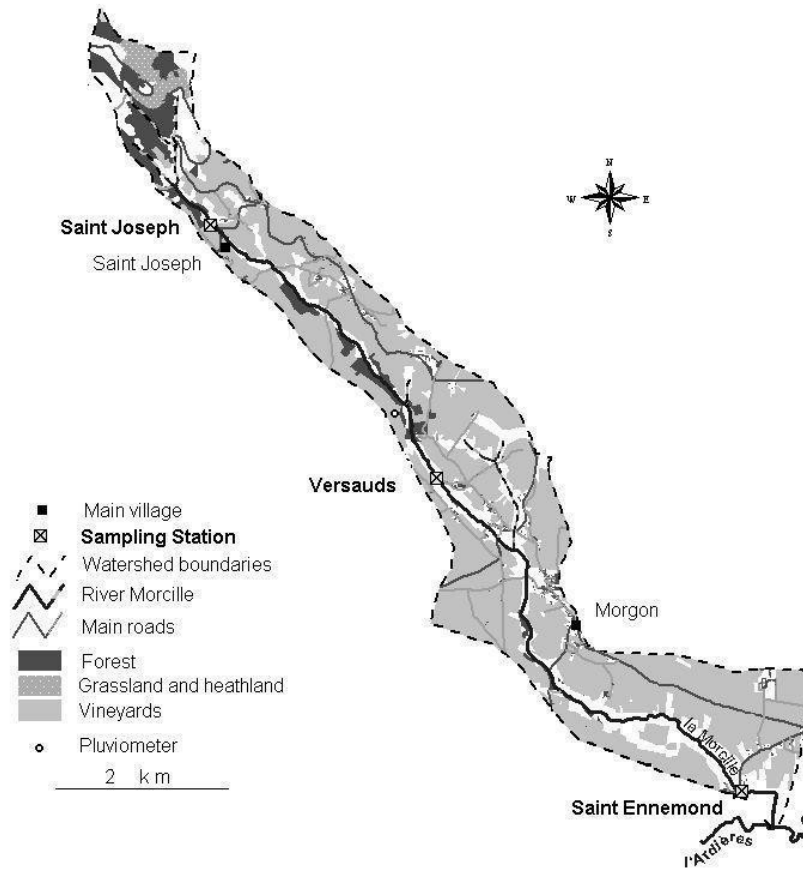
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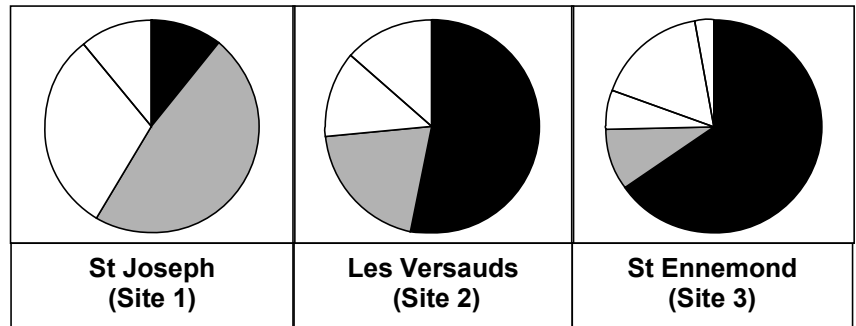
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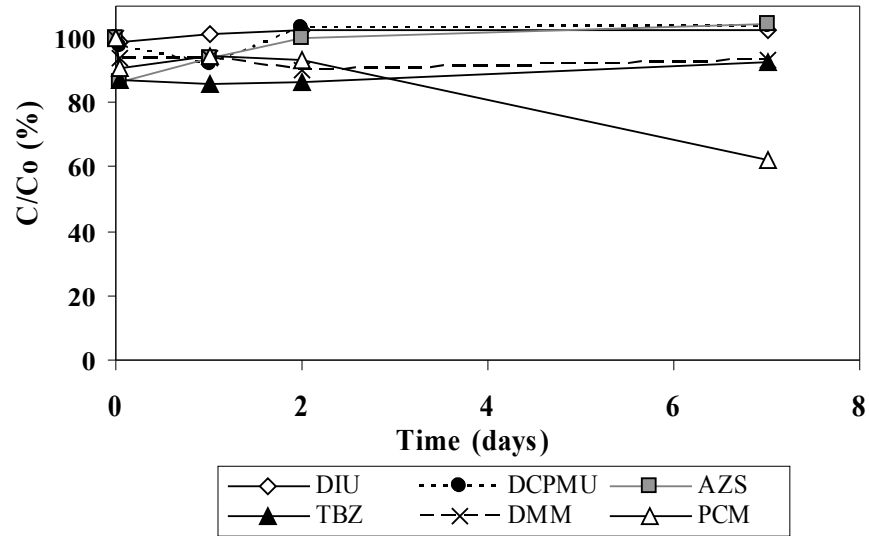


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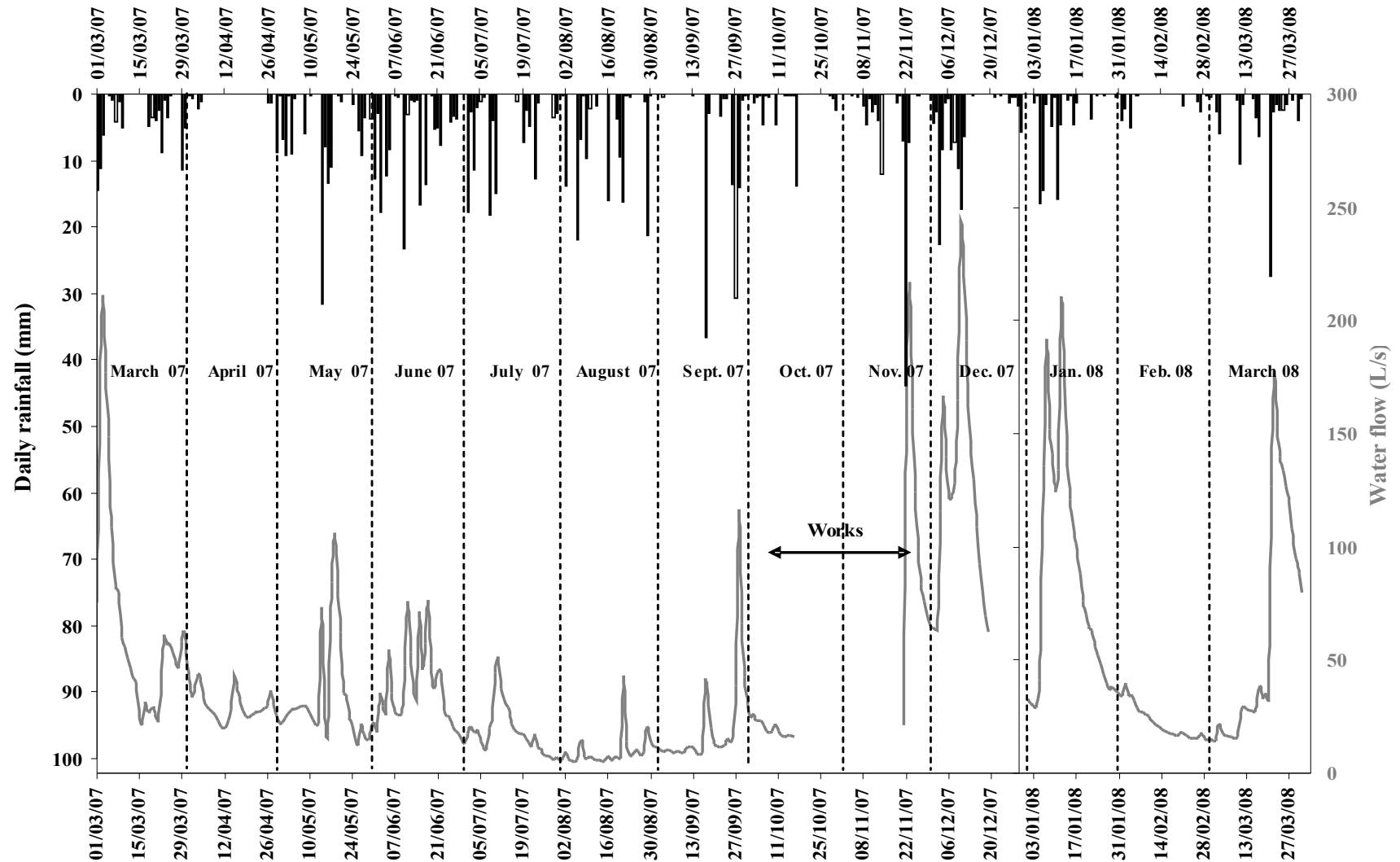
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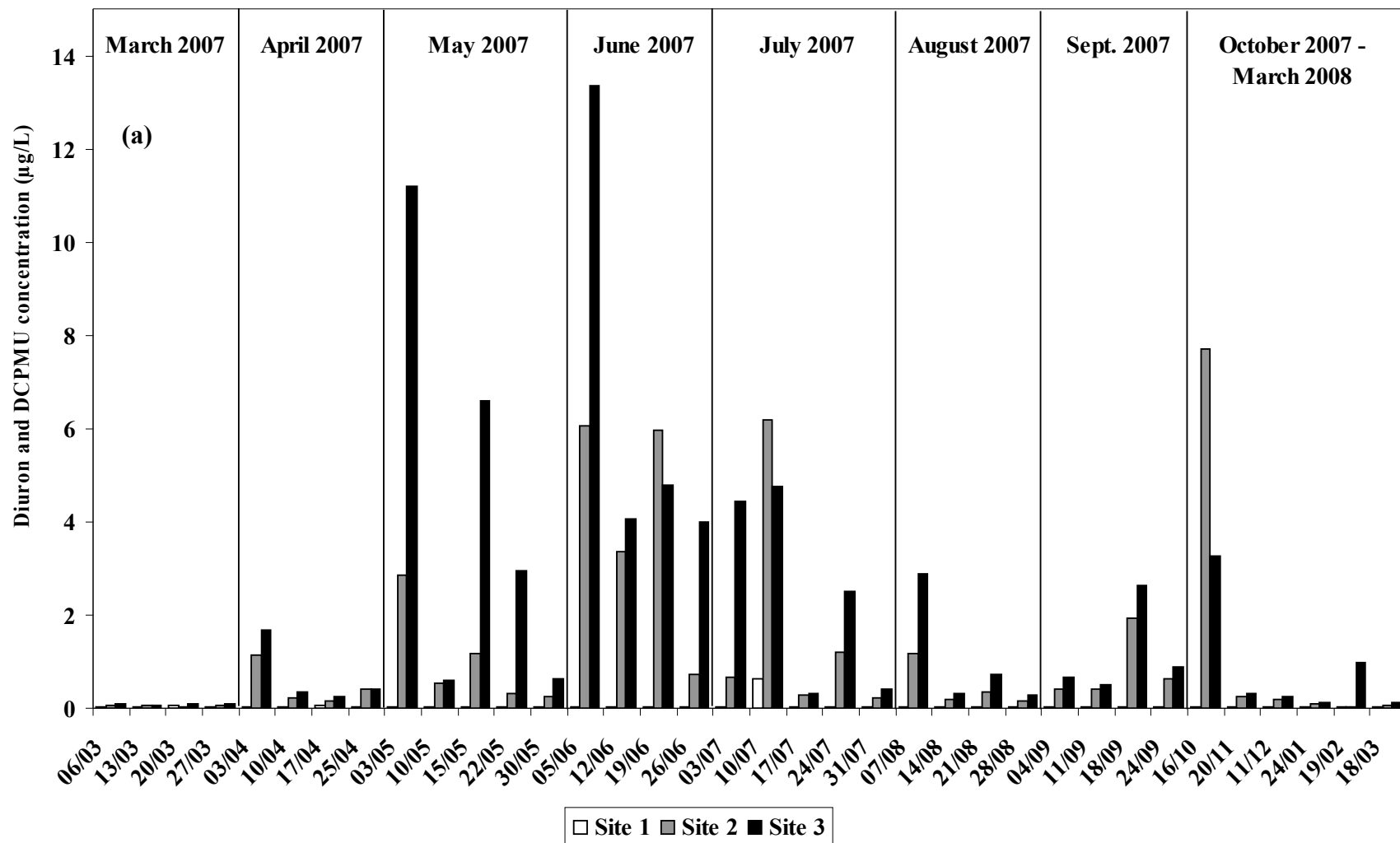
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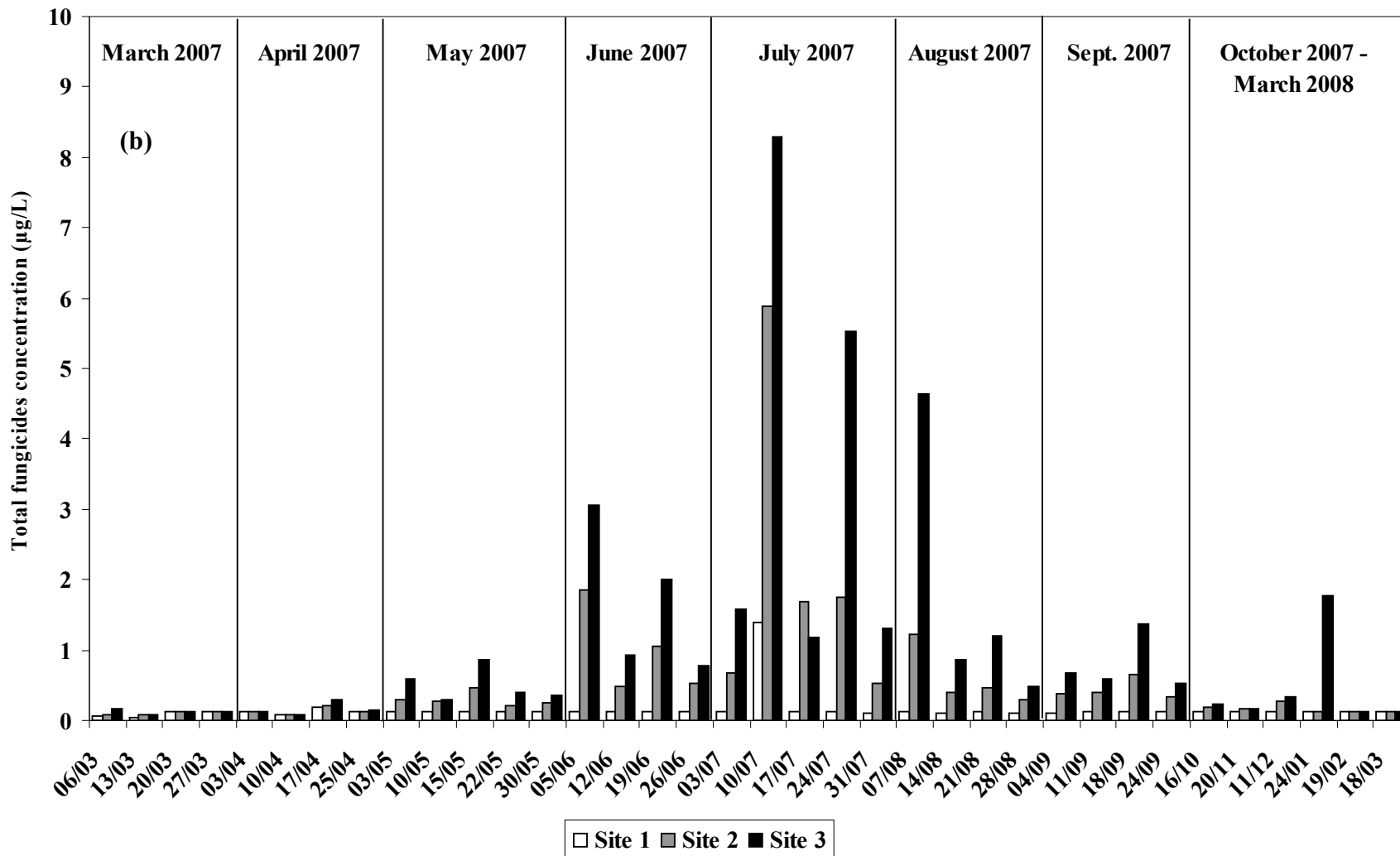
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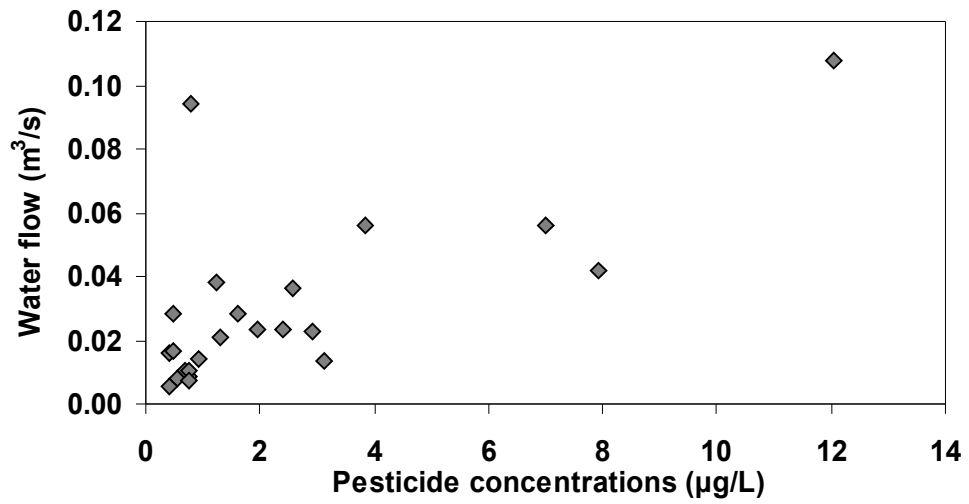
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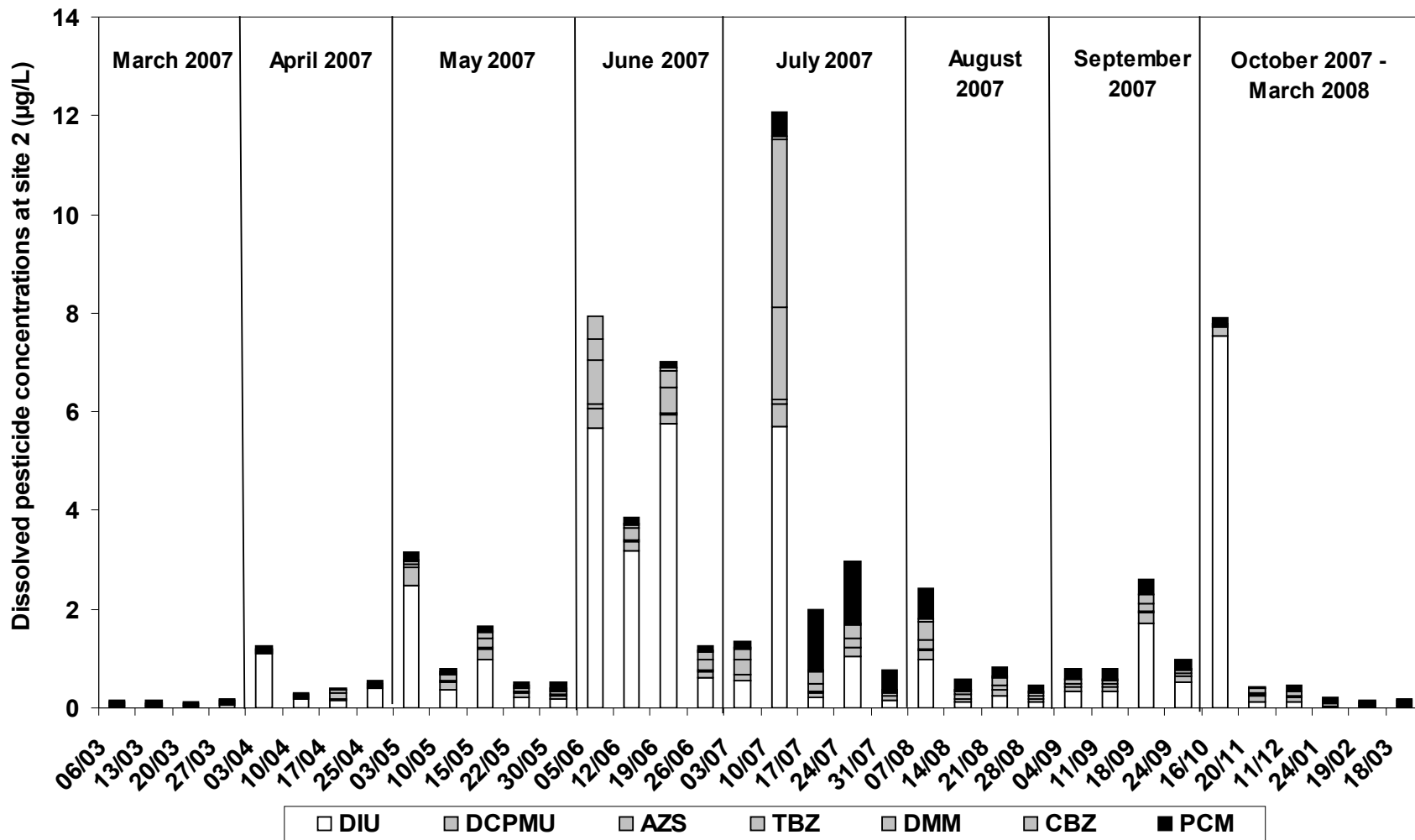


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694 Figure 6. Water flow (m³/s) versus total pesticide concentrations (µg/L) in the Morcille

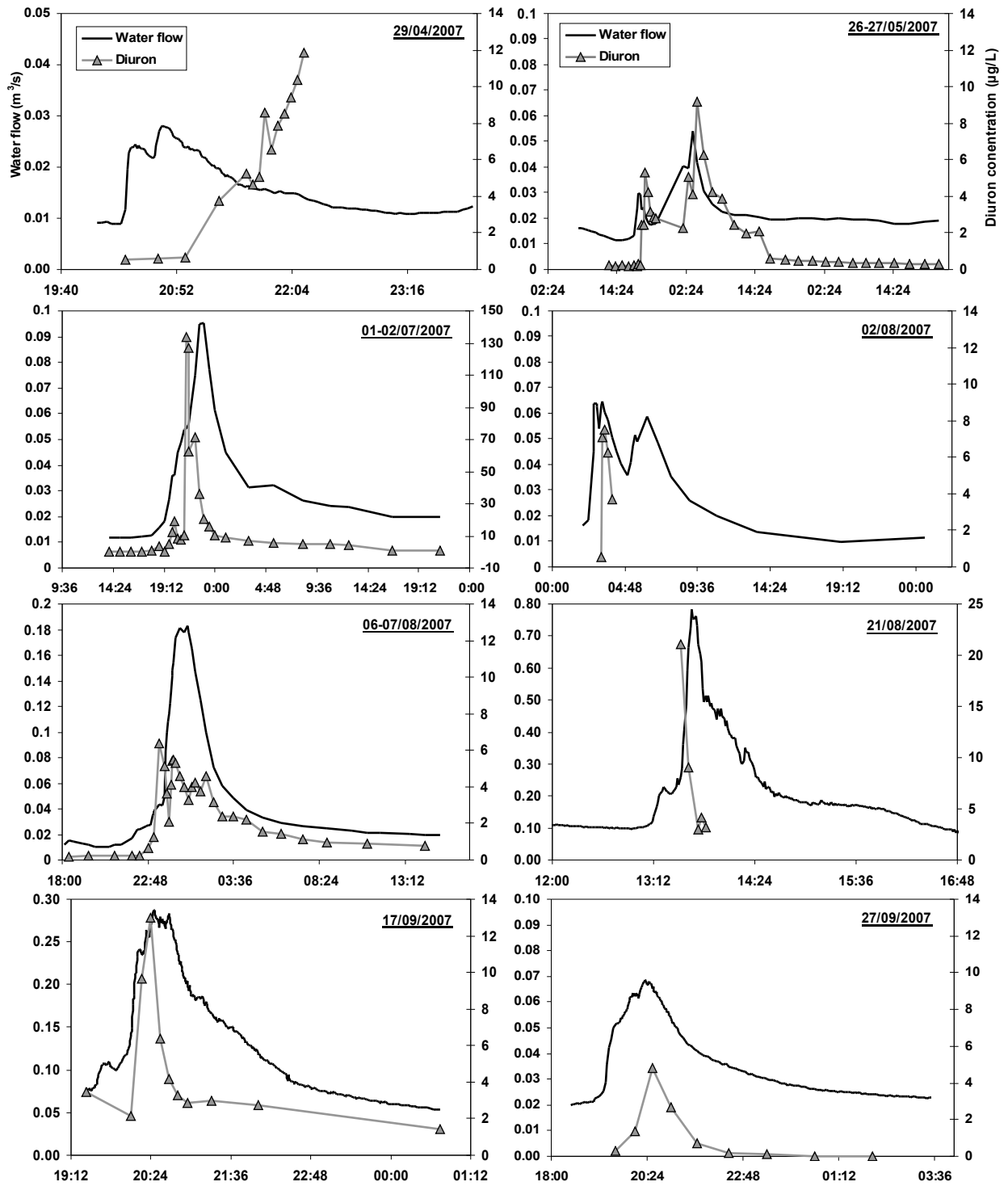
695 stream at site 2 during weekly monitoring (March 2007 to September 2007).

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698 Figure 7. Dissolved pesticide concentrations (µg/L) at site 2 from March 2007 to March 2008.



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700 Figure 8. Diuron concentrations (µg/L) and water flow (m³/s) at site 2 during flood events

701 for the April-September 2007 period.

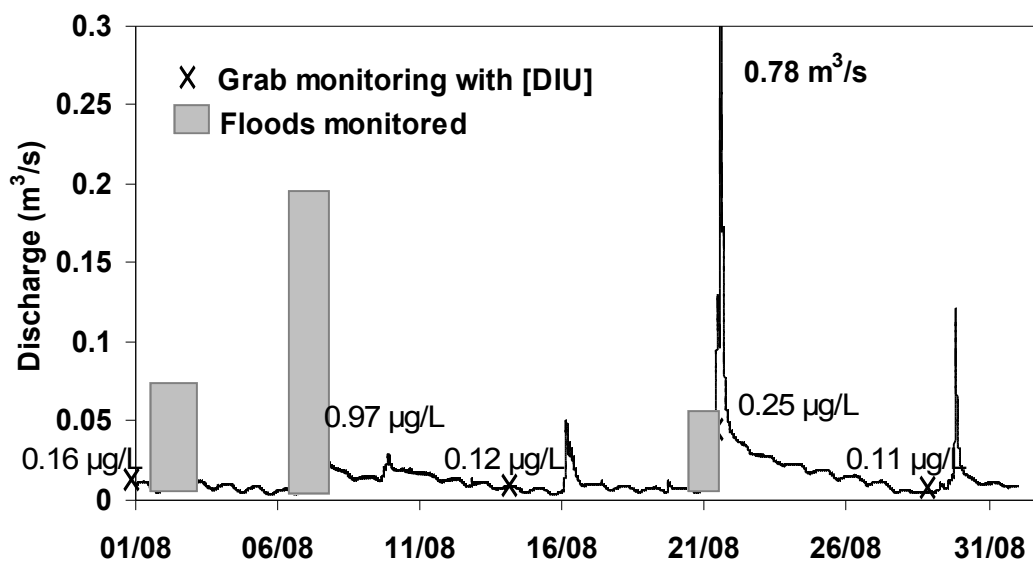
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709 monitoring of grab samples and floods in August 2007 (× : diuron concentration measured
710 using grab sampling).

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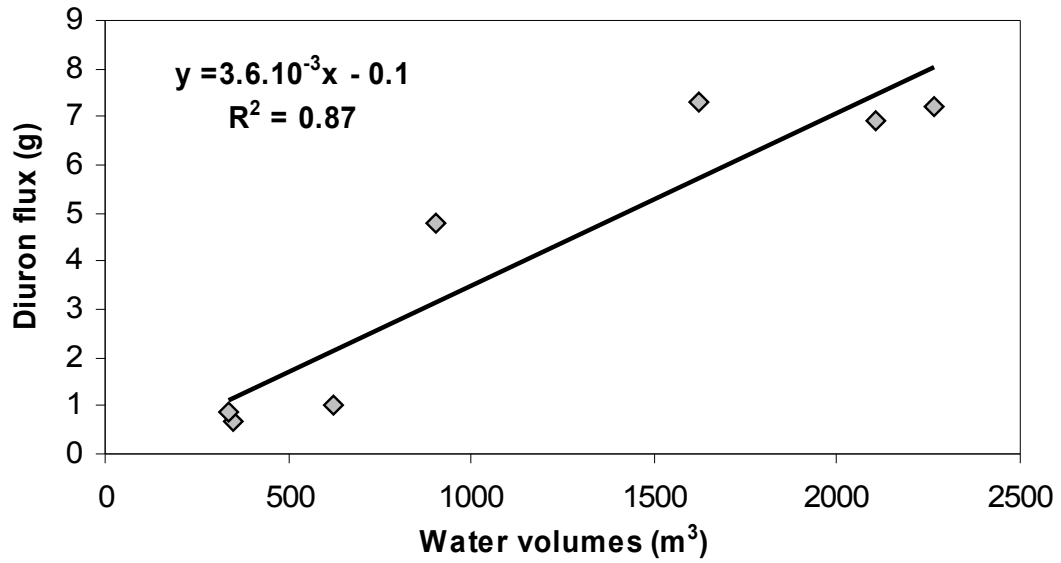
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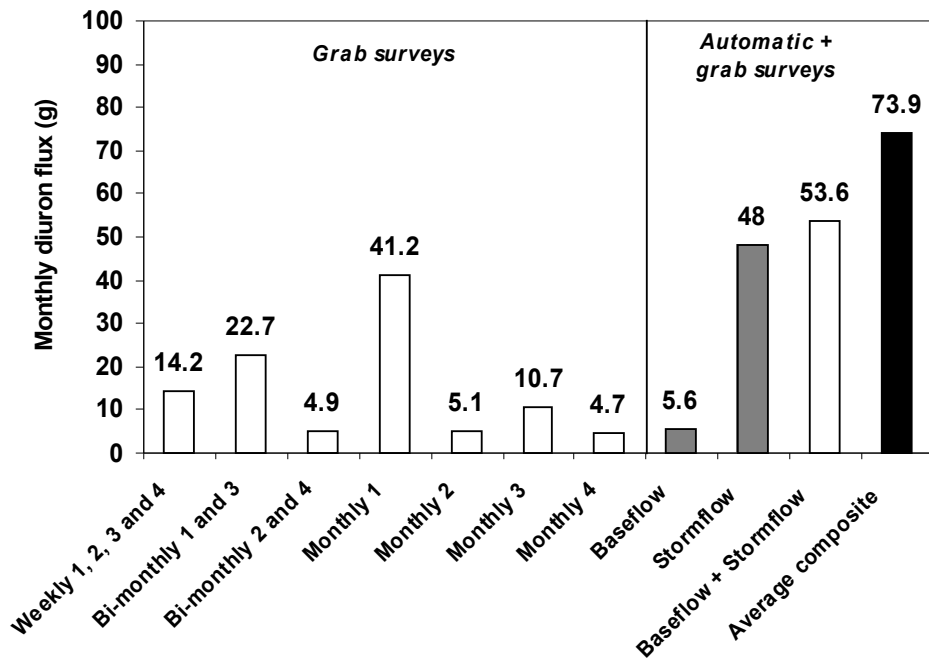
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738 Figure 10. Diuron flux (g) versus water volumes (m³) during 7 floods (site 2).

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773 Figure 11. Monthly diuron flux (g) at site 2 in August 2007, estimated using different
774 methods and monitoring data.

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776 **Table 1. Properties of the studied pesticides (Tomlin, 2000; AFSSA, 2008).**

Compound (abbreviation)	Category	Water solubility (mg/L)	Koc (L/kg)	Log Kow	Half life (days)
Azoxystrobin (AZS)	Fungicide	6.0	423	2.50	8.7-14
Carbendazim (CBZ)	Fungicide	8.0	200	1.56	30-150
Dimetomorph (DMM)	Fungicide	18.0	290-566	2.70	23-35
Diuron (DIU)	Herbicide	36.4	480	2.85	90-180
Procyimidone (PCM)	Fungicide	4.5	1514	3.14	28-84
Tebuconazole (TBZ)	Fungicide	32.0	803-1251	3.70	43-170

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778 **Tableau 2. Annual pesticide fluxes in g and g/Ha and percentage of exportation in the Morcille stream**

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Pesticides	Annual flux(g)	Annual specific flux (g/Ha)	Annual recommended amount (g/Ha) (Couteux and Lejeune, 2007)	Percentage of exportation (%)
DIU	1335	7.60	1500	0.57
DCPMU	167.7	0.96	-	
AZS	31.7	0.18	250	
TBZ	223.8	1.28	70	
DMM	164.0	0.94	250	
CBZ	52.0	0.30	105	
PCM	180.0	1.03	750	
Total	2154	12.30		

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781 **Tableau 3. Maximal pesticide concentrations (µg/L) and fluxes (g) for each monitored flood at site 2.**

		DIU	DCPMU	AZS	TBZ	DMM	CBZ	PCM
29/04/2007	Cmax (µg/L)	11.9	1.09	0.13	0.60	0.10	0.10	0.27
	Flux (g)	0.477	0.023	0.0008	0.011	0.079	0.0005	0.027
26/05/2007	Cmax (µg/L)	5.30	0.30	0.43	0.32	0.75	0.10	0.14
	Flux (g)	0.68	0.064	0.057	0.057	0.084	0.015	0.040
27-28/05/2007	Cmax (µg/L)	9.20	0.60	0.54	1.01	0.82	0.12	0.23
	Flux (g)	6.91	0.59	0.46	1.02	0.55	0.13	0.26
01-02/07/2007	Cmax (µg/L)	134.0	0.71	0.14	6.50	14.4	0.16	1.30
	Flux (g)	45.5	0.98	0.14	5.00	6.80	0.24	1.50
02/08/2007	Cmax (µg/L)	7.50	-	-	-	-	-	-
	Flux (g)	0.89	-	-	-	-	-	-
06-07/08/2007	Cmax (µg/L)	6.40	0.79	0.08	1.41	2.81	0.28	3.17
	Flux (g)	7.21	1.08	0.082	1.50	3.67	0.28	3.49
21/08/2007	Cmax (µg/L)	21.1	-	-	-	5.98	-	-
	Flux (g)	4.80	-	-	-	1.3	-	-
17/09/2007	Cmax (µg/L)	13.0	-	-	-	-	-	1.40
	Flux (g)	7.33	-	-	-	-	-	0.193
27/09/2007	Cmax (µg/L)	4.80	-	-	-	-	-	-
	Flux (g)	1.01	-	-	-	-	-	-

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793 **Table 4. Comparison of calculated and estimated diuron flux (g) during floods at site 2.**

Flood eve	Calculated diuron flux (g)	Water volumes (m³)	Estimated diuron flux (g)	Bias (%)
26 May 2007	0.68	348	0.80	13
27-28 May 2007	6.91	2106	7.1	3
02 August 2007	0.89	335	0.70	-19
06-07 August 2007	7.21	2263	7.70	6
21 August 2007	5.88	1970	6.60	12
17 September 2007	7.33	1619	5.30	-27
27 September 2007	1.01	621	1.70	73

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