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1 **Pesticide contamination pattern of surface water in an urban–agricultural**
2 **Mediterranean watershed (Wadi Guenniche, Bizerte Lagoon, Northern Tunisia)**

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10 **Abstract**

11 Two years of monthly sampling and hydrological monitoring were performed at the
12 outlet of a Mediterranean watershed in northern Tunisia to determine the contents of 469
13 pesticide active ingredients and metabolites in water and evaluate their behavior. Wadi
14 Guenniche is a tributary of the Bizerte coastal lagoon, with a watershed area of 86 km², which
15 exhibits pluvial cereal, legume, and orchid cultivation and irrigated market gardening. Twenty-
16 nine pesticide active ingredients and 2 metabolites were detected in water. Twenty-four
17 pesticide active ingredients were authorized for use in Tunisia. Among them, 14 had never been
18 mentioned in previous farmer surveys. Five herbicides and their metabolites were the most
19 frequently detected: aminomethylphosphonic acid (AMPA) (100%), glyphosate (94%),
20 simazine (94%), 2,4-D (70%), and deisopropylatrazine (DIA) (47%). The detection frequency
21 and concentration range suggested that the phytosanitary pressure and resulting water
22 contamination are close to those on the northern Mediterranean shore. These results, in addition
23 to characterizing the pollution state, emphasized the need for additional studies on the use and
24 fate of pesticides on the southern shore of the Mediterranean Sea, particularly in Tunisia.

25

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30 **KEYWORDS:** Pesticides; water fluxes; water contamination; agricultural practices; southern
31 Mediterranean bank; Bizerte Lagoon; Wadi Guenniche; Tunisia.

34 **Introduction**

35 Pesticides are used for plant protection for agriculture, disease vector control for public
36 health and maintenance of urbanized areas ^[1]. Once spread across large surfaces, multiple active
37 ingredients may cause water contamination by parental compounds and their metabolites ^[2].
38 As seen in many parts of the world, water contamination can cause environmental stress, thus
39 decreasing biodiversity, ^[3] and harm humans through the contamination of food and drinking
40 water ^[4]. Moreover, the combined effects of different contaminants may enhance environmental
41 stress and health problems through the interaction of multiple pesticide ingredients and
42 metabolites; ^[5] thus, the coexistence of multiple contaminants is an important issue.

43 The situation varies between countries on the northern shore of the Mediterranean Sea,
44 where European Union directives promote extensive public monitoring and studies on
45 numerous pesticide substances in water bodies, and southern countries, where limited or no
46 information is available to the public or the scientific community^[6]. The high cost and/or low
47 availability of analytical measurements have led to little interest in public monitoring. Water
48 body contamination by pesticides is presumably lower due to the smaller amount of pesticides
49 used by Tunisian farmers than in northern countries and because of the drier and warmer climate
50 with intermittent streams that favor retention and degradation upon transport. Nevertheless, the
51 occurrence of environmental issues in hot spots, such as the Bizerte Lagoon, has triggered
52 studies focusing on the use and detection of pesticides in sediments, organisms and surface
53 water bodies. Farm surveys near Ichkeul Lake and Bizerte Lagoon have estimated pesticide
54 use^[7-9]. The estimated cereal and fodder area of 113390 ha was treated with 22.7 tons of
55 pesticide products, corresponding to 5 active ingredients belonging to the herbicide class
56 [iodosulfuron (1ton), fenoxaprop (2.6 tons), 2,4-D (2.3 tons), mesosulfuron (0.6 tons) and
57 glyphosate (2.8 tons)], 2 active ingredients belonging to the fungicide class [tebuconazole (4.6
58 tons) and epoxiconazole (8.8 tons)] and one insecticide [deltamethrin (0.3 tons)].

59

60 Another study reported farmer surveys identifying 20 fungicides, 2 insecticides, and 17
61 herbicides applied in the lagoon watersheds south of Bizerte (Tinja and Menzel Bourguiba)^[10].
62 In the same study, the use of polar organic chemical integrative sampler (POCIS) technology
63 allowed the detection of 22 pesticide substances in three wadis and lagoon waters. However,
64 pollutant flows into the lagoon could not be estimated since the study did not consider water
65 level monitoring and no water flow was determined; indeed, the only information provided by
66 the POCIS was average concentrations. Moreover, legacy pesticide contents belonging to the
67 organochlorine chemical family (18) were measured in lagoon sediments, including DDT
68 metabolites, $\alpha,\gamma,\beta,\delta$ -HCHs, α -endosulfan, heptachlor and its metabolites, dieldrin, endrin, and
69 its metabolites, and aldrin^[8]. In the Bizerte Lagoon water, acetochlor, alachlor, diuron and two
70 degradation products were detected, namely, N-(3,4 dichlorophenyl)-N-(methyl)-urea and N-
71 (3,4 dichlorophenyl)-N-(methyl)-urea, deisopropylatrazine (DIA), linuron and simazine^[11]. In
72 2020, the Tunisian list of authorized active ingredients for agricultural use ^[12] included 232
73 active ingredients (excluding minerals, bacteria, pheromones, conditioners, and growth
74 controllers) encompassing more than 1000 formulations. Due to the diversity of pesticide
75 products available to farmers and the limited analysis capability, previous southern
76 Mediterranean studies focused on a very small number of pesticide ingredients, which may not
77 reflect the real contamination state. Knowledge of the active agricultural ingredients used by
78 farmers should aid in the selection of the studied analytes while considering toxicity,
79 occurrence, and scientific interests and considering their technical availability and budget. This
80 approach may generate blind spots. First, legacy contamination may be caused by active
81 ingredients applied long ago and thus cannot be targeted by existing practice surveys. Second,
82 important ingredients, such as glyphosate, may be difficult to analyze at local laboratory
83 facilities and/or may be too costly to analyze in multiple samples. Third, the use of pesticides

84 in urban areas (i.e., not for agriculture) is not often examined. Uses for pesticides in urban areas
85 may include residential and facility treatments for disease vector control (cockroaches, fleas,
86 flies, mosquitos, rodents, etc.), vegetation control (in parks, roads, streets, tracks, etc.) and
87 fungicide treatments of materials (wood, textiles, etc.). To reduce these blind spots, it is possible
88 to implement multiresidue analysis methods that allow the analysis of a water sample with a
89 quantification limit (QL) of $0.01 \mu\text{g L}^{-1}$ for 469 pesticide ingredients and metabolites. These
90 methods are not commonly applied in developing countries such as Tunisia and may highlight
91 new contamination concerns.

92 The objective of this work was to characterize the contamination of surface water by
93 pesticide active ingredients and their metabolites and to target the largest number of analytes
94 available, within the context of a typical Mediterranean watershed with agricultural and urban
95 activities. By combining monthly water sampling data with continuous flow measurements
96 collected over more than two years, we aimed to relate available agricultural practices to the
97 contamination pattern.

98 **Materials and methods**

99 *Site description*

100 We selected wadi Guenniche (Figure 1) as an inflow tributary of the Bizerte Lagoon because it
101 potentially carries multiple contaminants resulting from agricultural and urban activities. The
102 watershed covers an estimated area of 86 km^2 and is representative of coastal plains with a
103 slight slope less than 1% surrounded by higher slopes, reaching an altitude of 401 m above sea
104 level (asl) (Figure 1). The El Alia district area included in the watershed accounts for 82% of
105 the total watershed area. The city of El Alia is located in the upper part of the watershed, and
106 according to the 2014 Tunisian census, the population of the city was 18,359 inhabitants.
107 Notably, outputs of rain drainage networks occasionally presenting black waters for the cities

108 of El Alia and Khetmine were reported^[13]. In fact, a 1.2 km cemented open canal exits El Alia
109 town on the northeastern side (37°10'5.42"N, 10°0'37.02"E) following Farhat Hached Street
110 (Figure 1). This collector frequently experiences sewage water flow, with a flow rate of
111 approximately 10-50 L s⁻¹. The collector is connected to the main course of the wadi that
112 reaches the Bizerte Lagoon 8.81 km away. A few small villages, namely, Khetmine,
113 Magheraoua, and Hariza, are distributed in the lower parts of the city, which comprises a
114 cultivated plain with agricultural drains connected to the wadi.

115 *Watershed land use*

116 Agricultural data ^[14] for El Alia district allowed us to approximate the following characteristics
117 of the Guenniche watershed: a forest cover area of approximately 1700 ha, a constructed area
118 of approximately 200 ha, and a pasture area of 100 ha. The remaining area (cultivated land) is
119 approximately 6600 ha. For the other districts around the lagoon reported by Mhadhbi et al. ^[10],
120 cereals (wheat, oat, barley, and triticale) account for 68% (4500 ha) of the surface area, fodder
121 (fenugreek, ray grass, triticale, and colza) accounts for 5.5% (363 ha) of the surface area, and
122 legumes account for 12.7% (838 ha) of the surface area. Notably, in 2018, 92200 tons of cereals,
123 14100 tons of fodder, 35000 tons of legumes, and 8100 tons of beans were produced in El Alia
124 district ^[15]. Moreover, El Alia district exhibited notable fruit (average: 7000 tons) and citrus
125 (average: 3400 tons) tree production covering an area smaller than 400 ha. Similarly, olive trees
126 (1057 tons of olive oil) cover an area of approximately 1100 ha but were often cultivated in
127 combination with cereals. At the scale of the Bizerte governorate, the yields varied between 2.4
128 and 2.9 tons ha⁻¹ for wheat, between 1.5 and 2.5 tons ha⁻¹ for barley and between 1.8 and 2.8 tons
129 ha⁻¹ for triticale ^[15]. These yield ranges are consistent with the estimated area of 4500 ha
130 dedicated to cereals in the Guenniche watershed and the 2018 production level. To establish a
131 correlation between the growing season and the presence of pesticides in water bodies, it is
132 important to consider the agricultural calendar in Tunisia. Legumes (peas, beans, chickpeas,

133 etc.) are cultivated from the end of October (sowing) to the end of April (harvest). Cereals
134 (wheat, oat, barley, etc.) are cultivated from October–November (sowing) to June (harvest).
135 Vegetable crops (melons, cucumbers, potatoes, tomatoes, etc.) are cultivated from March–April
136 to June–July (harvest), and fruits are grown throughout the year (Table 1S). Applying the
137 recommended doses of the main active ingredients to estimated areas of the different crop
138 categories provided an estimation of the amounts spread yearly in the watershed (Table 1).

139 *Hydrological description of wadi Guenniche*

140 Daily precipitation data were downloaded from reanalysis datasets of the European Centre for
141 Medium-Range Weather Forecasts ^[16] and compared to data obtained from the station nearest
142 Bizerte Airport (37°15'00"N, 09°47'59"E). The annual total precipitation during the 2-year
143 monitoring period was 594 mm from 2019–2020 and 559 mm from 2020–2021. The second
144 year was globally drier but had higher monthly precipitation in December (188 mm in 2020
145 compared with 91 mm in 2019) (Figure 2). According to Bizerte delegation data, cereal
146 production was 2.7% greater during the 2021 harvest, with a similar wheat yield. However, the
147 barley and triticale yields increased by 47% and 16.7%, respectively, emphasizing the
148 importance of December precipitation.

149 The hydrological station and sampling site are located at the last bridge before the lagoon
150 (37°10'24.55"N, 9°56'41.80"E). The wadi course from the station to the lagoon is 1.85 km
151 long. The monitoring station contained a water level measurement device with a LevelTroll[®]
152 probe TROLL 200 with a piezoresistive sensor. Data were acquired at 10-min intervals from
153 the 10th of May 2019 to the 18th of August 2021. The control section was an old concrete slab
154 at the point where the old road crosses the wadi, and the relationship between the water level
155 and the flow in the section was calibrated by flow measurements at 5 different water levels
156 using a portable magnetic flow meter (Flow-Mate Cometec[®]). The measurements were repeated
157 three times during the water-falling phase. The flow was extrapolated between points along the

158 flow section using the Manning equation. In this work, the flow measurements were integrated
159 on a daily basis. The measured flow rates ranged from 12 to 1443 L s⁻¹. Analysis of the daily
160 stream time series was performed using the in-line hydrograph separation tool Sephydro, and
161 (<https://sephydro.hydrotools.tech/>) the local minimum method was applied^[17]. During the
162 studied period, base flow accounted for 68% of the total stream; thus, 70% of the daily flow
163 rates were lower than 100 L.s⁻¹ (Figure 2). Compared with the usual Mediterranean hydrologic
164 behavior, the wadi never dries in summer. This phenomenon may be explained by 3 water
165 contributions: i) drainage inputs from irrigated fields, ii) underground water, and iii) permanent
166 urban wastewater inputs from El Alia city and small villages. Short-term flood events are
167 generally caused by rain. Moreover, the larger amount of December precipitation impacted the
168 streams. Notably, the monthly averages were 149 and 383 L s⁻¹ for December 2019 and
169 December 2020, respectively. The yearly stream averages were 89.4 and 152.1 L s⁻¹ for the
170 2019–20 and 2020–21 hydrologic cycles, respectively. Streamflow accounted for 5.5% and
171 9.9% of the total precipitation during the 2019/2020 and 2020/2021 hydrological cycles,
172 respectively. The short-term correspondence between rain events was studied using the cross-
173 correlation between the daily precipitation and daily wadi streamflow. The average hydrogram
174 response unit (Figure 3S) indicated a continuous correlation between one day before and 14
175 days after rain events. Four days after a given rain event, the significant (p>95%) correlation
176 was less than 0.2, indicating a quick return to the base flow conditions.

177 ***Water sampling and chemical analysis***

178 A total of 548 ingredients were mentioned in this study (Tables 4S-1-5]). Ingredients belonged
179 to one or more of the four following groups: 1) the 233 active synthetic ingredients authorized
180 in Tunisia^[12]; 2) the 38 active ingredients mentioned by farmers during the surveys reported in
181 previous studies^[8-10]; 3) the 469 analytes considered by the multiresidue analysis protocol
182 (Table 4S,5S,6S); 4) detected 31 molecules in water (Table 6S). The results of the contingency

183 analysis are reported in Table 2. Only 154 (66%) of the active ingredients authorized for use in
184 Tunisia could be analyzed because analytical methods for these ingredients were not available.
185 This phenomenon reflects one of the limitations of this study: despite the 469 analytes
186 considered, 78 potential contaminants were beyond the detection scope.

187 Water sampling was performed on a monthly basis in the wadi, with some gaps due to COVID-
188 19 lockdowns and travel restrictions (Figure 2). The Guenniche watershed output location was
189 not adequate to secure the installation of an automatic time-regulated or stream-regulated
190 sampling device. Indeed, all the sampling was punctual and was performed between 8:30 and
191 9:30. Twenty samples were collected during the study period: 17 samples were collected at the
192 wadi monitoring point, one sample was collected in the nearest traditional well, one sample was
193 collected at the output of the cemented canal, and one sample was collected in a tributary of the
194 Guenniche watershed, i.e., the wadi Helia. The samples were stored in 1-L glass bottles (for
195 multiresidue analysis) and 150-mL plastic bottles (for glyphosate and aminomethylphosphonic
196 acid (AMPA) analysis) at -18°C, and they were transported within 48 hours in iceboxes two
197 times a year by car and boat from Tunis (Tunisia) to Montpellier (France). The samples were
198 subsequently processed at La Drome Departmental Laboratory
199 (<https://www.ladromelaboratoire.fr/en/the-laboratory/>) by a dedicated transporter to ensure the
200 cold chain. Notably, 469 pesticide active ingredients and metabolites (Tables 5S-[1-4]) were
201 analyzed according to ISO standards N° 10695, 6468, 11369, and 12918 and EPA methods N°
202 507, 508, and 625. MultipH liquid/liquid extraction was performed, followed by gas and/or
203 liquid chromatography by instruments coupled with different detectors (diode array detector,
204 electron capture detector, flame ionization detector, ion trap and tandem mass spectrometry
205 device). For glyphosate, AMPA, and glufosinate, ISO standards N° 21458 and 16308 were
206 applied, and information on the methods used was summarized (Tables 5S-[1-4])

207 **Provisional load estimates**

208 Monthly sampling cannot represent the short-term variation in contents that may be driven by
209 runoff events and treatments. However, we proposed to estimate provisional river annual loads
210 for the most frequent analytes for the following reasons: 1) Importance of base flow implied
211 that direct runoff episodes were limited in time and volume; thus, the hydrological behavior of
212 the watershed indicated intervention of large buffering capacity; and 2) Samplings were taken
213 outside flooding events with flow stream values less than 150 L s^{-1} . 3) No significant correlation
214 was detected between the wadi discharge values at the sampling time and the pesticide
215 concentrations in the water on one hand or between the discharge values and salinity on the
216 other hand. We computed daily linear interpolation of the contents ($\mu\text{g L}^{-1}$) between the 17
217 punctual samplings. Each interpolated value was multiplied by the daily stream value (L d^{-1})
218 load results were reported in (Table 6S). In some cases, a laboratory report may indicate the
219 presence of an analyte in the sample at a concentration lower than the QL. In such instances,
220 the concentration used for daily interpolation was $\text{QL}/3$. If the analyte was not mentioned in the
221 report, the values were set to 0. To determine the influence of the QL on the annual budget, we
222 computed the annual substance flow according to this limit. Considering a mean annual flow
223 of $3.5 \cdot 10^6 \text{ m}^3 \text{ y}^{-1}$ and analytes with QL values of 0.01, 0.02 or $0.05 \mu\text{g L}^{-1}$, contaminant annual
224 loads that could be neglected would be less than or equal to 0.035, 0.070 or 0.175 kg y^{-1} ,
225 respectively.

226 *Temporal and seasonal analysis*

227 The serial time arrangement of the detected substances was obtained on the basis of the
228 sampling dates ^[18] using seriation date-constrained mode in the Past4[®] software results were
229 reported in Table 7S.

230 **Predicted no-effect concentrations**

231 The predicted no-effect concentration (PNEC) for fresh water may provide a relative toxicity
232 benchmark for each substance regarding its impact on biota. The lowest PNEC values are
233 constantly being updated because they depend on toxicological experimental data for each
234 substance and organism and model application. Nevertheless, whenever the detected
235 concentration of a given substance in a water body is equal to or greater than the corresponding
236 PNEC, a priority warning should be issued. We gathered lowest PNEC values for fresh water
237 from the Norman database ^[19] and compare them to the maximum concentration reached in the
238 wadi water.

239

240 **Results and discussion**

241 *Detected pesticide active ingredients and metabolites*

242 During the survey, 31 pesticide active ingredients and metabolites were quantified in the water
243 samples, 3 of which were detected only in city wastewater (Table 6S). In contrast, 7 analytes
244 detected in the water samples did not belong to the list of authorized ingredients for agricultural
245 use in Tunisia (Table 2, Table 4S-1). Two of them were metabolites of authorized ingredients
246 (DIA and AMPA obtained from the degradation of simazine and glyphosate, respectively), and
247 4 unauthorized active ingredients detected were not mentioned by the farmers' surveys. In
248 addition, 14 (58%) of the 24 authorized ingredients detected in the water were not mentioned
249 by the farmers' surveys. These results indicated that local farmer surveys could not effectively
250 delimit potential active ingredient water contamination. On the one hand, these analytes may
251 be related to urban origins. On the other hand, this finding could encourage authorities and
252 scientists to include the largest list of substances in contamination diagnostics and not
253 exclusively rely on farmer interviews and/or authorization lists.

254 *Concentrations reached in stream water*

255 The range of concentrations of active ingredients and metabolites is reported in Figure 3, with
256 analytes sorted by the maximum concentration observed in the wadi samples. The same figure
257 also indicates the average, minimum, and maximum contents, as well as the standard error of
258 the mean. Six analytes of concern were detected, with concentrations higher than $0.5 \mu\text{g L}^{-1}$:
259 three herbicide active ingredients (2,4-D, glyphosate and simazine), 1 metabolite from
260 herbicides (AMPA), and one fungicide with only one detection (fludioxonil). Moreover, the
261 concentrations of 16 active ingredients exceeded the threshold of $0.1 \mu\text{g L}^{-1}$. Notably, the
262 maximum contents of 4 herbicides (metribuzin, mesosulfuron, chloroturon, florasulam) and
263 one metabolite with 8 detections (DIA), two fungicides (methomyl, flusilazole) and 4
264 insecticides (acetamiprid, clethodim, alphamethrin, permethrin) ranged from $0.1\text{--}0.5 \mu\text{g L}^{-1}$.
265 Then, 14 active ingredients with maximum contents in the range of $0.1\text{--}0.02 \mu\text{g/L}$ were
266 quantified, among which carbendazime, propamocarb, and metalaxyl were the most frequently
267 detected, with 6, 7 and 3 quantifications, respectively.

268 No organochlorine pesticide was detected in this study, indicating that persistent organic
269 pollutant (POP) water contamination does not occur at concentrations higher than the LQ (0.01
270 $\mu\text{g L}^{-1}$) in the wadi. Recently, analyzing DDT in water with an LQ 100 times lower in the
271 Mejerdha River^[20] allowed DDT quantification with a maximum content of $0.027 \mu\text{g L}^{-1}$ and
272 an average of $0.009 \mu\text{g L}^{-1}$. In an oasis in the Kebili region^[23], the DDT water content reached
273 $0.0015 \mu\text{g L}^{-1}$, with an average of $0.0006 \mu\text{g L}^{-1}$. In the drainage waters of Cap Bon citrus
274 orchards^[21], the DDT concentration reached $0.044 \mu\text{g L}^{-1}$, with an average of $0.023 \mu\text{g L}^{-1}$.
275 Moreover, DDT was quantified in other matrices, such as soil irrigated with treated wastewater
276 near Nabeul^[22] and locally in Bizerte Lagoon sediments^[9] and fish^[23], accompanied by HCH.

277

278 **Frequency and leachability of ingredients**

279 Among the 17 wadi water samples, 116 detections were observed : 79 were associated with 11
280 herbicides and their metabolites, 27 were associated with 11 fungicides, and 10 were associated
281 with 7 insecticides. Nine analytes were detected more than 2 times, and these substances can
282 be considered regular contaminants (Figure 4). The frequency of detection and concentration
283 of active ingredients are often related to their specific characteristics, which describe their
284 ability to degrade and be retained in the soil. For instance, the groundwater ubiquity score^[24]
285 (GUS) is commonly used as a leachability index that describes the mobility of an active
286 ingredient released from the soil (see Table 2S for K_{oc} and DT_{50} values used) .

287 For negative GUS values, all the analytes had fewer than 3 quantifications, most of which were
288 insecticides. In fact, all the detected insecticide ingredients had GUS values lower than 0.9, and
289 their average or single concentrations were lower than $0.3 \mu\text{g L}^{-1}$. The analytes quantified more
290 than 5 times had GUS values in the range of [0.9-4.82], which corresponded to low to high
291 leachability. Five of them were herbicides, and their metabolites had average concentrations
292 higher than $0.09 \mu\text{g L}^{-1}$; two of them were fungicides with average concentrations in the range
293 of [0.03-0.04] $\mu\text{g L}^{-1}$. Nevertheless, 13 ingredients had the same range of GUS values, with
294 fewer than 3 detected. In conclusion, negative GUS values corresponded to chemical
295 characteristics that constitute a potential mobility threshold. The low and moderate
296 leachabilities of glyphosate and AMPA were sufficient, in this context, to favor a high
297 frequency of detection and high concentrations. High leachability favored an elevated number
298 of detections (>8) for the other main herbicides and metabolites (simazine, 2,4D and DIA).

299 *Frequency and treatment doses*

300 The frequency of detection was associated with the estimated amount applied (Table 1) to the
301 watershed, assuming the recommended dose for the corresponding ingredients and metabolites
302 (Figure 5). A linear trend linked the logarithm of the estimated applied amounts to the number
303 of detections ($R^2=0.78$). This trend indicated that, at the watershed scale, the occurrence of these

304 contaminants was more easily related to the doses applied than to their retention and
305 degradation characteristics. Glyphosate is used as a total herbicide that can be applied
306 throughout the year since it is registered for all culture types. Glyphosate is frequently used in
307 urban areas to clear vegetation from railways, backyards, streets, etc. Moreover, the application
308 dose for plants (12 L ha^{-1} , with a product concentration of 360 g.L^{-1}) in agricultural or urban
309 activities could explain the considerable amount reaching the lagoon. Moreover, we determined
310 an AMPA concentration of $5.56 \mu\text{g L}^{-1}$ in the wastewater output of El Alia, emphasizing the
311 city's contribution to the total contamination level. The provisional loads of the Guenniche
312 watershed output included a glyphosate load of 2.57 kg y^{-1} and an AMPA load of 12.6 kg y^{-1}
313 (Table 6S). The presence of AMPA is due to the degradation of glyphosate by either biological
314 or chemical pathways. Moreover, as the mole weight of glyphosate is 1.67 times that of AMPA,
315 the total amount corresponds to 23.7 kg y^{-1} of the initial amount of glyphosate exported.
316 Reported to the area of the watershed the load was 2.7 g ha^{-1} . This value is close to the 3.11 g
317 ha^{-1} observed in Argentina for a study in a larger watershed^[25]. For 23060 kg of the
318 recommended dose, the export ratio would be approximately 0.1%. This ratio clearly agrees
319 with the values reported in the literature. For instance, glyphosate applied in a 2.2 ha catchment
320 vineyard in western France was detected during 20 runoff events between 2009 and 2012, for
321 an export coefficient of 0.33% ^[26]. Moreover, at a French vineyard scale of 42 ha, pesticide
322 losses were consistently less than 1% and even less than 0.1%. Notably, the glyphosate export
323 coefficient varied between 0.009% and 0.033% ^[27].

324 While it is banned for use in Europe, simazine remains authorized for agricultural use in
325 Tunisia. This herbicide active ingredient is recommended for peas and legumes. Thus, it may
326 be useful in peri-urban gardens. The authorities recommend the addition of 1.5 L ha^{-1} of a
327 product with a simazine concentration of 0.5 kg L^{-1} , corresponding to an amount of 0.75 kg ha^{-1}
328 ¹ of simazine (Table 1), and the treatment is applied two times a year. The annual application

329 within an area of 838 ha should correspond to a spread amount of 1257 kg y⁻¹. The computed
330 provisional load of simazine in the wadi output was 0.627 kg.y⁻¹. The export ratio reached
331 approximately 0.05%. In a 2320 ha watershed in Ontario, Ng et al. [28] reported a simazine
332 export value of 0.816 g ha⁻¹ y⁻¹ in runoff water. If applied to 838 ha with a 100% treated area of
333 peas and legumes, this could result in a 0.683 kg y⁻¹ runoff load that is relatively close to our
334 estimates. A recent study^[29] reported that a 5-year treatment resulted in an average simazine
335 load of 1.28 g ha⁻¹ y⁻¹ in different Salt River basin subwatersheds (USA). The authors advocated
336 that simazine load data could provide a reliable proportion of treated areas. In our case, a rate
337 of 1.28 g ha⁻¹ applied to 838 ha with a 100% treated area resulted in a value of 1.072 kg.y⁻¹,
338 indicating that the export ratio between the simazine surface load treatment and the
339 corresponding outlet flux was lower but of the same order as that in the US.

340 DIA is a metabolite produced from simazine and atrazine by both chemical and biotic
341 degradation [30]. The latter was not authorized for use in Tunisia in 2020^[12]. This metabolite has
342 been frequently detected in northern aquifers [30] but also around the Mediterranean Sea [31,32]
343 in southern bank countries such as the Gaza strip [33] due to its notable persistence in
344 underground waters. The presence of DIA may not necessarily indicate the actual use of
345 atrazine or simazine, as this metabolite may be stored in aquifers for a long time and could be
346 obtained through chemical or biotic degradation. The main DIA flow occurred in summer and
347 thus may be related to the contribution of contaminated underground waters to the wadi in the
348 absence of surface runoff.

349 2,4-D is a selective herbicide found in wastewater samples and is commonly used to eliminate
350 broadleaf weeds and most commonly affects cereal crops. The recommended dose for two
351 treatments on a 4500 ha area could reach 5830 kg y⁻¹ (0.9 L ha⁻¹ by 0.72 kg L⁻¹ by 2 on 4500 ha).
352 The estimated load of the wadi output of 2,4-D was 1.67 kg y⁻¹, resulting in an export ratio of
353 0.03%. This ratio was lower than those reported in the literature. For instance, reported export

354 ratios of 1.53%, 0.37%, and 0.06% during successive events from corn cultivated plots in
355 coastal Georgia (USA) treated with 0.56 kg ha⁻¹ were reported [34]. More recently, on a golf
356 course, an export value of 0.5% was obtained [35].

357 *Seasonal pattern*

358 A clear seasonal pattern was observed in the chemical analysis data, and the number of
359 detections and variety of analytes differed among the various seasons (Figure 6). In winter,
360 most of the detected compounds originated from the applied herbicides, with the greatest
361 variety. Twenty-four of the 29 detected substances originated from the 11 herbicides and their
362 metabolites. Before sprouting and during cultivation (in the interbank area), systemic herbicides
363 (glyphosate for cereals or atrazine for legumes) may be applied mostly in winter and spring.
364 During cultivation, largely in spring, for pluvial crops and irrigated fields, selective herbicides
365 (2,4D, clethodim, etc.) are applied. The amount and variety of herbicides detected decreased in
366 autumn, spring and summer to reach a minimum number of detections in summer, where 6
367 herbicides were detected in 15 detections. The smallest number of detections in the wadi course
368 in summer was due to the small surface area affected by the treatments and because rainfed
369 soils exhibited the driest state, and precipitation could not easily initiate runoff. This result
370 agrees with the outputs of glyphosate and AMPA measured in the Saone River (a tributary of
371 the Rhone River), where the smallest amount was registered during the summer season [36].

372 Fungicide active ingredients were particularly common in the wadi in spring, when the largest
373 number of analytes was observed (8) with the highest detection number (9). Similarly,
374 insecticides were more frequently detected in spring, but during autumn and winter, they
375 exhibited the lowest detection rates and the lowest variety levels compared to the other classes
376 of pesticides. Indeed, insecticides and fungicides are applied to fruits, legumes, and foliar
377 systems at the end of the cycle in spring and summer.

378 *Comparison of the two years*

379 The sampling period (from July 2019 to the end of May 2021) corresponds to two agricultural
380 periods for each product. This observation explains the presence of analytes exclusively at the
381 beginning (clethodim, carbendazim, propamocarb-HCl, acetamiprid, and DIA) or at the end of
382 the monitoring period (cypermethrin, tebuconazole, etc.) (Table 7S). The concentrations during
383 these two periods are also distinct from the stream values because the end of 2020 and the
384 beginning of 2021 exhibited more flood events. Fifty percent of the average daily flows were
385 lower than 57 L s^{-1} from July 2019 to July 2020 and 82 L s^{-1} from July 2020 to July 2021. We
386 considered that the 2020–2021 stream flows were influenced more notably by the contributions
387 of black water stemming from the city of El Alia, which altered the contamination pattern, as
388 described in past studies ^[37,38]. Indeed, higher chlorpyrifos and permethrin concentrations were
389 found in black water originating from the city canal and in the watershed outputs during the
390 second hydrological cycle. Permethrin is an insecticide authorized as a biocide for veterinary
391 and home use against fleas and lice but is not allowed for field use. Chlorpyrifos is an insecticide
392 authorized for agricultural use but is often used for gardening and residential purposes. Finally,
393 certain herbicides, such as glyphosate and its metabolites AMPA, simazine and 2,4-D, were
394 observed throughout the monitoring period. Small amounts can be issued from urban areas ^[38].
395 Propamocarb hydroxide and carbendazim are two fungicides that are applied mainly in summer
396 and autumn. Recommended treatments are usually performed at the last fruit or legume growth
397 stage, usually a few weeks before harvest. The two years of monitoring demonstrated that some
398 main active ingredients may be distinctly present during the first dry period relative to the
399 second hydrological period. For instance, the most frequently detected fungicides, carbendazim
400 and propamocarb, were detected from 2019–2020 but were not found in the samples collected
401 during the 2020–2021 rainy period. Acetamiprid was detected 4 times, mostly in spring (used
402 against leaf miner insects on citrus trees) and autumn (used against thrips on citrus plants).

403 Permethrin was mostly observed in summer and, in particular, in city black water, at relatively
404 high concentrations.

405 **Environmental risk pattern of Guenniche water**

406 PNEC values for freshwater were obtained from the Norman database network ^[18], and
407 the maximum concentrations in the Guenniche water samples and number of detections were
408 used for construction (Figure 7). The results demonstrated that 2,4-D and simazine attained
409 maximum concentrations greater than or equal to the lowest PNEC values (0.6 and 1 $\mu\text{g L}^{-1}$,
410 respectively), with high occurrence in the water samples. 2,4-D and simazine are known to have
411 acute (7 days) effects on aquatic plant biomass, with EC_{50} values of 2.7 and 0.3 mg L^{-1} ,
412 respectively^[33]. Moreover, simazine had an acute (72 hours) effect on algae growth (EC_{50} value
413 of 0.04 mg L^{-1}).

414 Regarding glyphosate and AMPA (the most frequently detected analytes), the maximum
415 concentrations measured in the Guenniche watercourse (at 2.23 and 23.3 $\mu\text{g L}^{-1}$, respectively)
416 were two orders of magnitude lower than the lowest PNEC values for each (120 and 1500 $\mu\text{g L}^{-1}$,
417 respectively). We reported a relatively high concentration of AMPA in Helia Wadi (76.6
418 $\mu\text{g L}^{-1}$), but the maximum concentration was less than the lowest PNEC. Nevertheless, as i) the
419 active ingredients glyphosate and AMPA are likely to generate unknown cumulative effects, ii)
420 numerous glyphosate products, including unevaluated toxic coformulants, may be present, and
421 iii) additional sensitive species should be considered in risk assessments, while environmental
422 toxicity evaluations should be updated in the coming years ^[39].

423 All the maximum contents of insecticides in the water were greater than the
424 corresponding lowest PNEC values, but the individual detection frequencies were low. These
425 contaminations, with maximum concentrations ranging from 0.02 to 1 $\mu\text{g L}^{-1}$, may be a concern

426 because they mostly occur during specific periods (summer 2019 and spring 2021). Thus, the
427 lowest PNEC thresholds of 2 to 3 insecticide active ingredients were exceeded at the same time.

428 In contrast, all fungicides demonstrated maximum content values lower than the lowest
429 PNEC values, with higher frequencies for certain fungicides, such as carbendazim. In the latter
430 case, the ratio decreased by one order of magnitude, and indeed, the maximum detected value
431 of $0.06 \mu\text{g L}^{-1}$ corresponded to a lowest PNEC value of $0.44 \mu\text{g L}^{-1}$. In a recent review, Zhou et
432 al. ^[40] advocated for enhanced quantification of the toxicological effects of carbendazim on
433 organisms under field conditions.

434 **Conclusion**

435 With more than 119 quantifications of 32 pesticide active ingredients and metabolites,
436 this study allowed us to characterize the detailed signatures of agricultural and urban water
437 contamination by pesticides in the Guenniche watershed and to rank the amounts of pesticides
438 reaching the Bizerte Lagoon. Multiresidue analysis was very effective in consolidating
439 contamination diagnostic approaches. No POPs were detected in Wadi Guenniche water during
440 the two-year monitoring period for an LQ equal to $0,01 \mu\text{g L}^{-1}$. With more specific and sensitive
441 analytical methods, DDT water contents were quantified at lower concentrations in Mejerdha
442 River^[22] and Cap Bon citrus orchard drainage waters^[23]. From our perspective, our encouraging
443 results demonstrated that DDT and HCH are not heavily used today in the Guenniche
444 watershed. These active ingredients have been banned in Tunisia since the end of the 1980s.
445 Indeed, POP pollution in sediments either originates from other watersheds or represents a
446 legacy phenomenon of the 1980s.

447 We detected 4 ingredients in water that were not authorized for use or mentioned in the
448 surveys. Furthermore, we detected 14 pesticide active ingredients authorized for use in Tunisia
449 but not mentioned in previous surveys. One limitation of this study is that 72 authorized active

450 ingredient could not be analyzed. Glyphosate and simazine and their quantified metabolites
451 (AMPA and DIA, respectively), accompanied by 2,4-D, were the main molecules involved in
452 water flow. This short list corresponds to the main cultivated cereals and legumes in the
453 watershed. DIA is a metabolite that corresponds to either the past use of atrazine or the actual
454 use of simazine for legumes. For the 5 leading molecules (glyphosate, AMPA, simazine, DIA
455 and 2,4-D), we estimated the order of magnitude of annual loads and compared them to
456 estimates of pesticide-recommended treatments in the main crop categories. For positive GUS
457 values, relative leachability differences between analytes were overridden by the relative
458 quantities of pesticide applied.

459 Our results represent the first attempt to understand pesticides stream outputs of a
460 coastal plain watershed on the southern Mediterranean bank during a two-year monitoring
461 period. We found that the relative behavior of the ingredients in surface water generally
462 corresponded to the literature, suggesting that pesticide treatment intensities and behaviors are
463 comparable on both sides of the Mediterranean. The behaviors of glyphosate and simazine were
464 compatible with the application of recommended doses in Tunisia on estimated surfaces. We
465 cannot assume that the use of glyphosate by farmers is very low, as stated in previous studies
466 [8,9]. For 2,4-D, the load and export ratio ranges were comparable to those of the treatments
467 quantified by Ben Salem et al. [8,9] and recommended doses. Apart from more frequently
468 detected herbicides, the detected ingredients and metabolites were not distributed evenly during
469 the two-year monitoring period. For instance, most insecticides were detected in the last
470 samples of spring 2021, indicating exceptional inputs from city wastewater and/or higher
471 stream values.

472 Finally, the results of this first multi-residue monitoring study conducted over two years
473 in the Guenniche watershed, which is characterized by a typical combination of agricultural and
474 urban activities, led us to recommend additional monitoring of the quality of surface water in

475 northern Tunisia. We acknowledge that the modest number of punctual samplings (17) and the
476 difficulty of maintaining an automatic sampler device on the wadi were significant limitations.
477 However, these initial results will help in the design of future studies in Tunisia by facilitating
478 the choice of substances to monitor and providing information on pesticide behavior and the
479 associated environmental risks. Indeed, within the socioeconomic and climatic contexts of
480 northern Tunisia, Bizerte Lagoon watershed water contamination triggered by recent
481 agricultural and urban activities should not promote less concern than that in the European shore
482 area. Moreover, neither smaller quantities of pesticides, nor lower ambient retention, nor
483 increased degradation limited the contamination of the wadi by the herbicides. AMPA,
484 glyphosate and 2,4D exhibited high contamination fluxes. These ingredients should be
485 specifically monitored in Tunisia, as they occur ubiquitously in the surface water of European
486 countries. Moreover, multiresidue studies combined with practice surveys and the use of
487 sampler devices should be recommended in other watersheds in northern Tunisia, particularly
488 near Beja, Bousalem, Kelibia, and Grombalia, to enhance the knowledge of the fate of
489 pesticides in water in these agroecosystems, thereby identifying problematic ingredients and
490 metabolites to eventually enforce specific laws and regulations.

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495 research organizations.

496 **Data availability statement**

497 The chemical data are presented in the supporting material (Table 8S). The daily hydrological
498 data that supported the flow estimates of the study are available from the authors upon
499 reasonable request.

500 **Disclosure statement**

501 The authors report that there are no competing interests to declare.

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FIGURE CAPTIONS

Figure 1. Locations of the Guenniche watershed and sampling points. The catchment area limits were delineated using SRTM data. El Alia district is a an administrative limit.

Figure 2. Daily streamflow ($L s^{-1}$) of wadi Guenniche, precipitation (mm) and number of sampling days during the monitoring period.

Figure 3. Concentrations of active ingredients and metabolites sorted by the maximum concentrations observed in the wadi Guenniche samples (average, minimum, maximum, standard error of the mean (Boxplots)). Numbers indicate the counts of quantifications when greater than 2.

Figure 4. Groundwater ubiquity score (GUS) and number of detected analytes. The diameter of the bubbles is proportional to the $\log_{10}([00* \text{ average concentration in } (\mu\text{g L}^{-1}))$. Green represents herbicides and their metabolites, brown represents fungicides, and red represents insecticides.

Figure 5. Estimated amounts of main active ingredients spread on the watershed (assuming recomanded doses) related to the number of detections observed. The diameter of the bubbles is proportional to the $\log_{10}([00* \text{ average concentration in } (\mu\text{g L}^{-1}))$. Green represents herbicides and their metabolites, brown represents fungicides, and red represents insecticides. The metabolites (DIA and AMPA) are associated to their mother ingredient (Glyphosate and simazine).

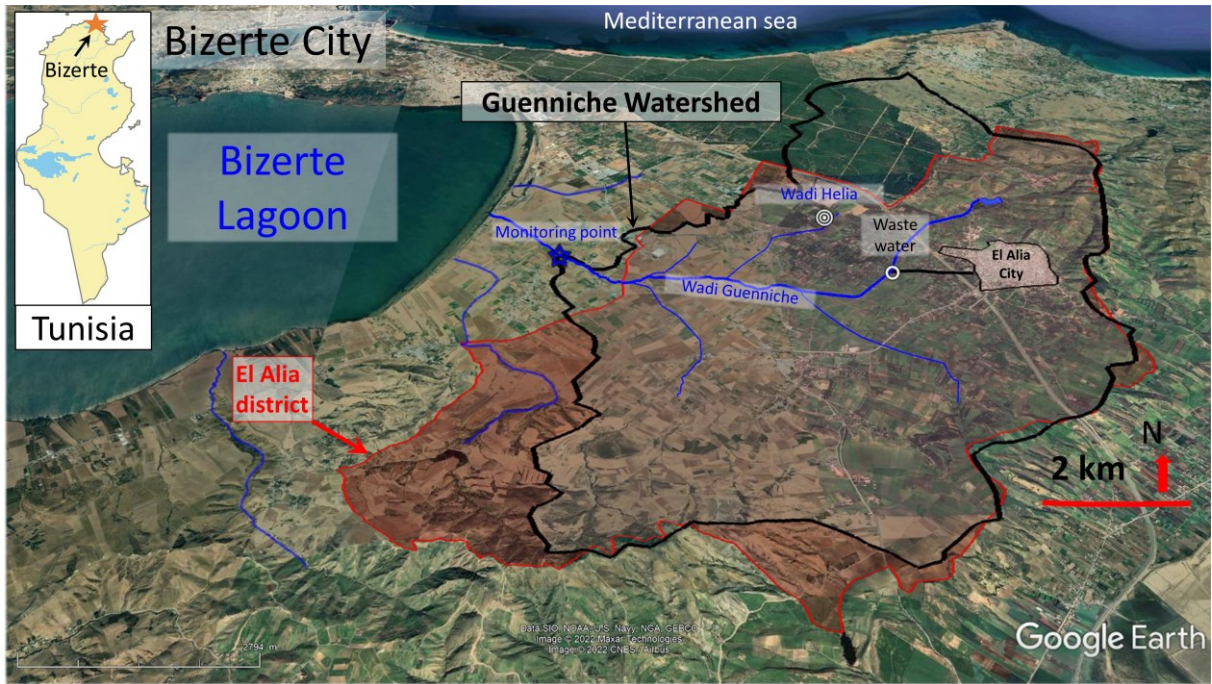
Figure 6. Number of detections of herbicides (and their metabolites), fungicides and insecticides in relation to the number of their different analytes and the sampling seasons. Green represents herbicides and their metabolites, brown represents fungicides, and red represents insecticides.

Figure 7. Maximum pesticide concentrations in fresh water and lowest PNEC values in the Norman database. The size of the bubbles is proportional to the number of detections. Green represents herbicides and their metabolites, brown represents fungicides, and red represents insecticides.

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682 Figure 1.

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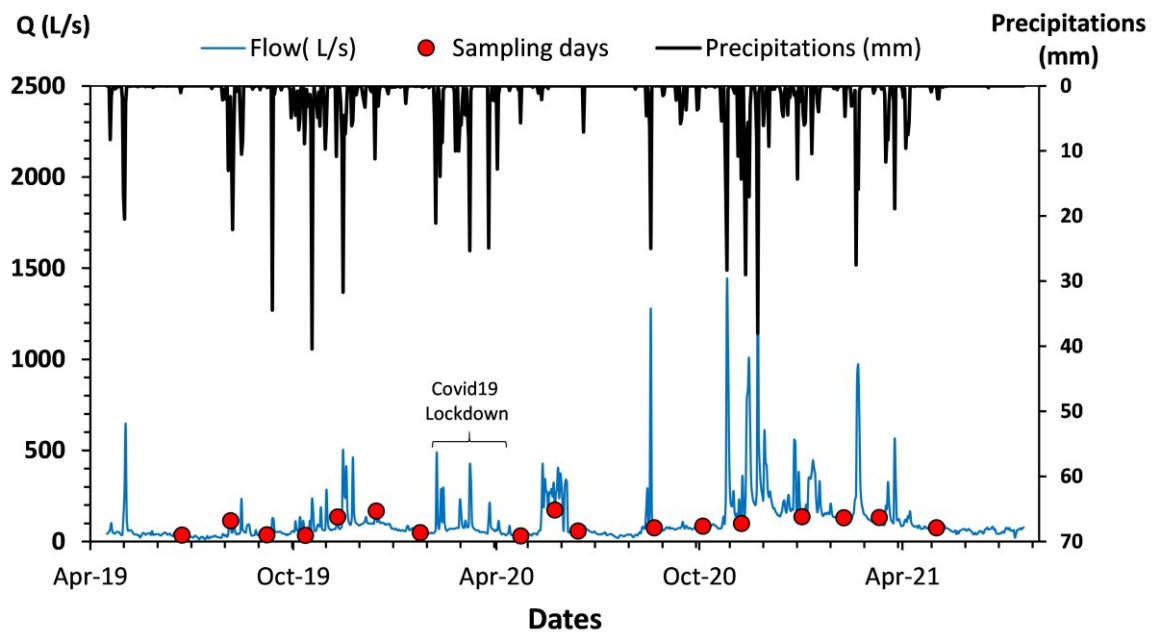
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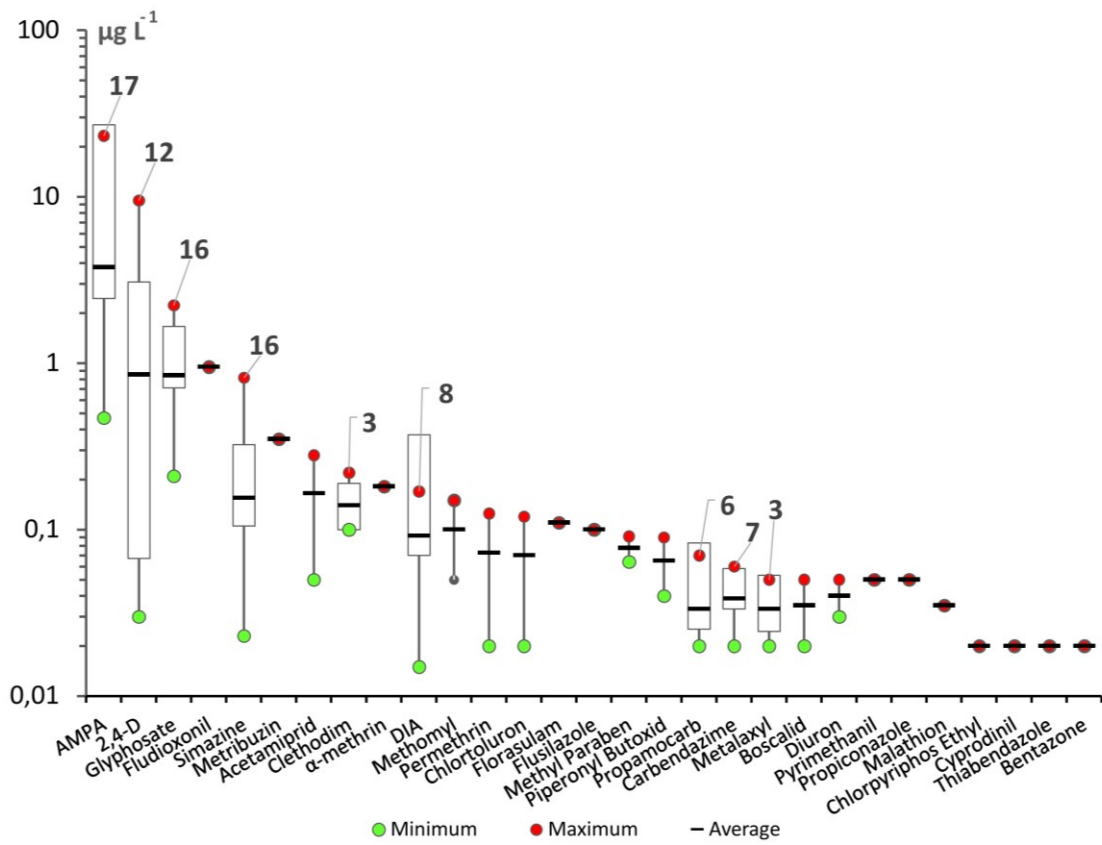
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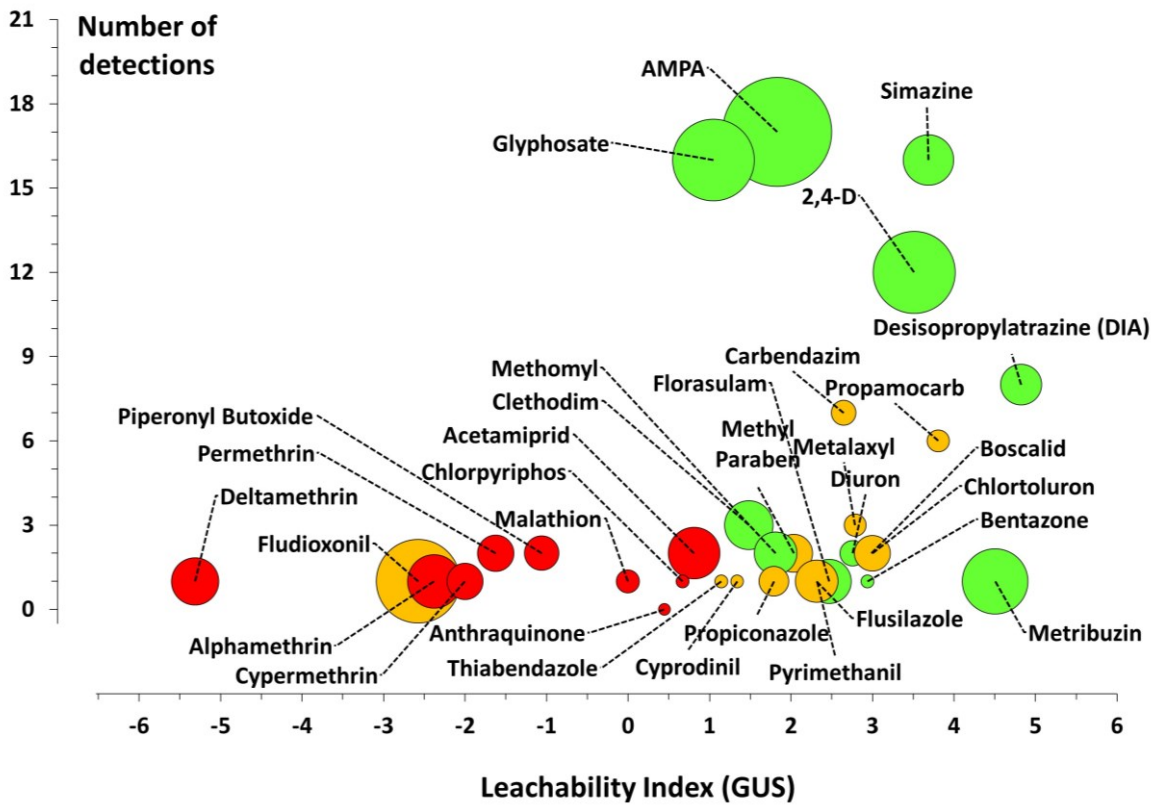


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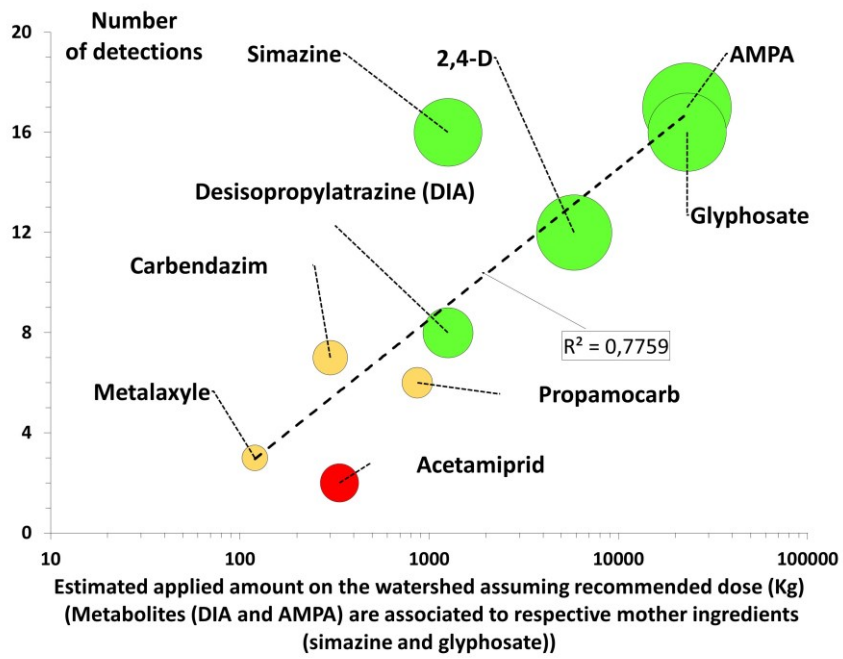


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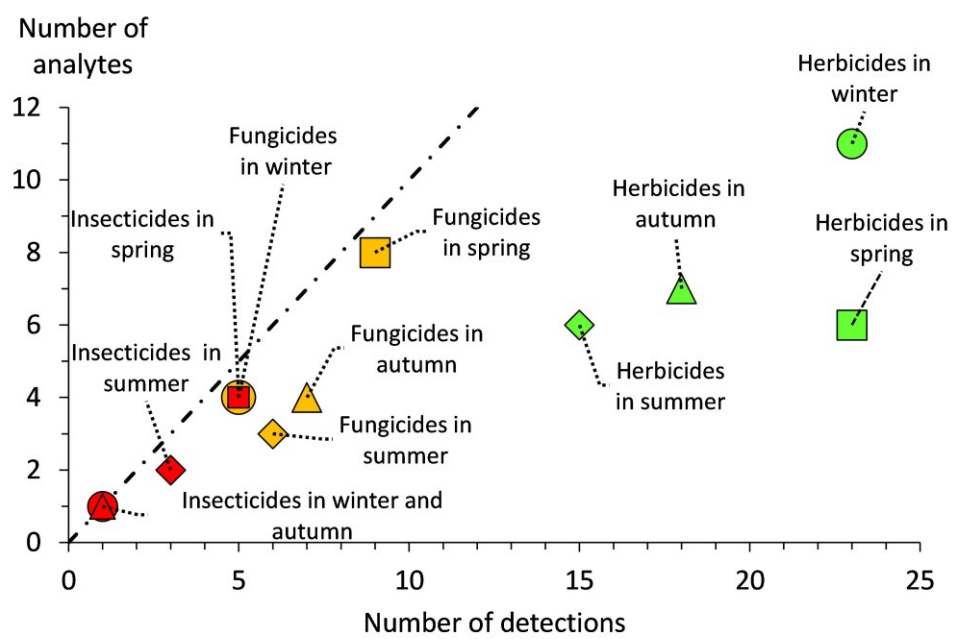


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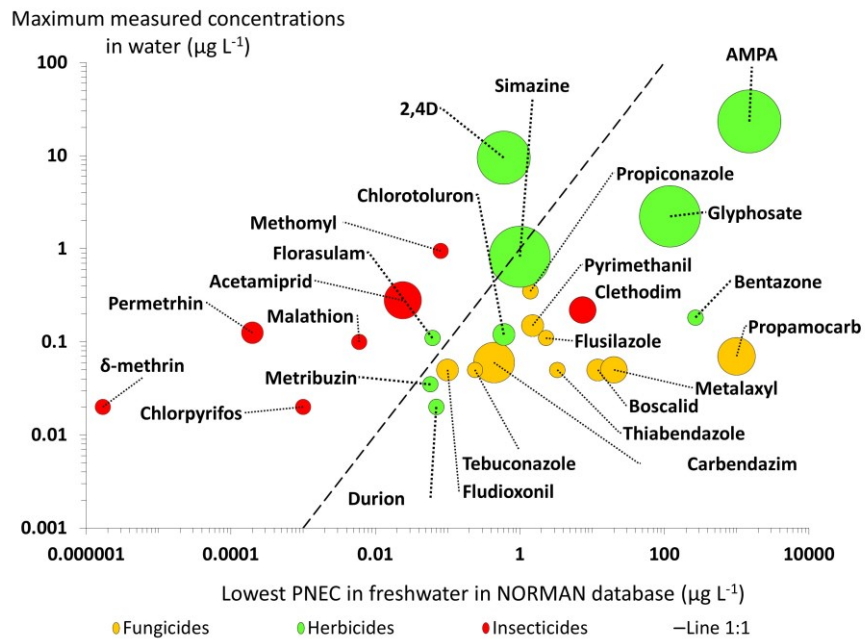
714 Figure 6.

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Figure 7.

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730 **Table 1** : Estimates of active ingredients supplies by year in the Guenniche watershed assuming
 731 application of recommended treatments and surfaces evaluation based on 2018 production.

Active ingredients Name	Crop category	Recommended treatments			Surfaces in watershed ha	Number of treatments By year	Resulting amounts Kg y ⁻¹
		L ha ⁻¹	kg L ⁻¹	Kg ha ⁻¹			
Glyphosate	Cereals & legumes	12	0.36	4.32	5338	1	23060
Simazine	Legumes	1.5	0.50	0.75	838	2	1257
2.4-D	Cereals	0.9	0.72	0.65	4500	2	5832
Propamocarb	Vegetables	2	0.72	1.44	300	2	866
Carbendazim	Fruit trees	0.5	0.50	0.25	600	2	300
Acetamiprid	Fruit trees	0.4	0.70	0.28	600	2	336
Metalaxyl	Vegetables	2.5	0.08	0.20	300	2	120

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735 **Table 2:** Overview of the pesticide active ingredients and metabolites considered: i) Authorized
 736 list of pesticides for agricultural use in Tunisia^[12.]; ii) Pesticide treatments mentioned by local
 737 farmers in the literature^[8.-10]; iii) Laboratory analytes' listing(Table 4S).; iv) Quantified active
 738 ingredients and metabolites of this study(Tables 4S & 8S).

Mention in farmers' surveys	Active ingredients not authorized in Tunisia and metabolites			Active ingredients authorized in Tunisia			Total
	Analyzed		Not analyzed	Analyzed		Not analyzed	
	<QL	>QL		<QL	>QL		
Ingredient mentioned	2	1	1	18	10	6	38
Not mentioned	306	6*	-	112	14	72	438
Total analyzed	308	7*	-	130	24	-	469
Total	315*		1	154		78	548

739 <QL = less than the quantification limit. >QL = above the quantification limit. * With 2 metabolites (AMPA and DIA)

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Supplemental material

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749 **Table 1S:** Main crops cultivated in the Guenniche watershed. period of cultivation and
750 example of authorized active ingredients; H: herbicide. F: fungicide. I: insecticide.

Crops	Growing period	Before sprouting	Interbank or foliar treatments	End cycle treatment Fruit and grain protection
Legumes	15 October–15 November until 15 April		clethodim (H). glyphosate (H) simazine (H)	
Cereals	15 October–15 November until 15 June	Glyphosate (H)	florasulam (H). 2.4-D (H). chlortoluron (H). bentazone (H). cypermethrin (I)	tebuconazole (F)
Vegetable crops	March to July April to June–July	Glyphosate (H)	clethodim (H). metribuzin (H). glyphosate (H). methomyl (I). cypermethrin (I). α -methrin (I)	fludioxonil (F). propamocarb (F)
Fruit trees	Perennial cultivation		glyphosate (H). methomyl (I). cypermethrin (I). α -methrin (I). acetamiprid (I)	cyprodinil (F). propamocarb (F)
Olive trees	Perennial cultivation		cypermethrin (I). malathion (I). chlorpyrifos-ethyl (I)	

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757 **Table 2S.** Active ingredients detected in water. Koc. Half-life from PPDB. Lgal status in
 758 Tunisia ^[12] and Europe (PPDB) agricultural use and example of doses.

Active ingredients detected in water	Koc PPDB *=INERIS §=SAGE L kg ⁻¹	DT ₅₀ [§] (PPDB typical or Field) Days	Legal status in Tunisia: “mentioned”. “or “not mentioned” in the 2020 list of authorized ingredients in Tunisia for agricultural use. If mentioned. target cultivations	Appro ved in CEE [§]	Doses L/ha.kg/ha. g/hl.cc/hl-g/L
AMPA	2002	419.0	Not mentioned Metabolite (from glyphosate)	Yes	
Glyphosate	1424	17.3	All cultivation. soil nude	Yes	12L/ha-360g/L
Simazine	130	90.0	Legumes	No	1.5l/ha
2.4-D (DIA)	39 69	28.8 170.0	Cereals Metabolite (from atrazine (not mentioned))	Yes No	0.4kg/ha
Propamocarb h.	41§	39.3	Cucumbers. melons. potatoes	Yes	200cc/hl- 722g/L
Carbendazime	223*	40.0	Fruits and apples trees	No	50cc/hl- 500g/L
Acetamiprid	200	3.0	Strawberries. apple and citrus trees	Yes	40g/2OOL
Metalaxyle	162	36.0	potato. tomato. circumbitaceous.	Yes	200cc/hl- 500g/L
Boscalid	772*	484.4	Vineyards. wheat. pear & apple trees	Yes	75g/hl-500g/l
Permethrin	100000	42.0	Not mentioned (Veterinary and urban)	No	-
Diuron	680	229.0	Not mentioned	No	-
Clethodim	8§	3.0	Peas. garlics. Onions	Yes	1L/ha-120g/L
Piperonyl Butoxide	89125	13.0	Not mentioned(Synergizer of pyrethrinoids)		-
Methyl Paraben	119*	11.4	Not mentioned (Food conservative)		
Chlortoluron	108*	33.5	Wheat	Yes	4.8L/ha-500g/L
Pyrimethanil	438§	50.9	Vineyards. tomatoes. strawberries. apples trees	Yes	250cc/hl-300g/L
Chlorpyriphos Ethyl	5509	386.0	Vineyard. Corn. tomato.Fig. Citrus & Apples trees	No	100cc/hl-480g/L
Cyprodinil	1550§	45.0	Apple pear & peach trees		50g/hl-500g/L
Fludioxonil	145405*	164.0	Potato seeds. Vineyards. Strawberry. Circumbit.	Yes	25%-60-120g/hl
Thiabendazole	3983	724.0	Wheat. barley	Yes	200cc/Q1 -25g/L
Florasulam	22	8.5	Wheat tricial. oats	Yes	0.75L/ha -1.5g/L
Methomyl	72	7.0	Market gardening. Corn	No	150g/hl-200g/L
Propiconazole	1086	71.8	Wheat barley.	No	0.8L/ha-124g/L
Flusilazole	1164	300.0	Not mentioned	No	-
Alphamethrin	288735	42.6	Beet. tomato. pears. fruits with glitches	No	30cc/hl-100g/L
Bentazone	55	20.0	Peas. wheat. fenugreek	Yes	4L/ha-480g/L
Malathion	1800	1.0	Vineyards. olive. citrus trees	Yes	500cc/ha-500g/L
Metribuzin	3	19.0	Potato. tomato. tobacco	Yes	700g/ha-750g/kg
Anthraquinone	3215§	8.0	Not mentioned	No	-
Cypermethrin	307558	22.1	Market gardening. olive. beet. wheat. corn. fruits	Yes	50cc/hl-250g/L
Deltamethrin	10240000	58.2	Tomato. apple tree. beet. cereals. potato. legume.	Yes	100cc/hl-25g/L

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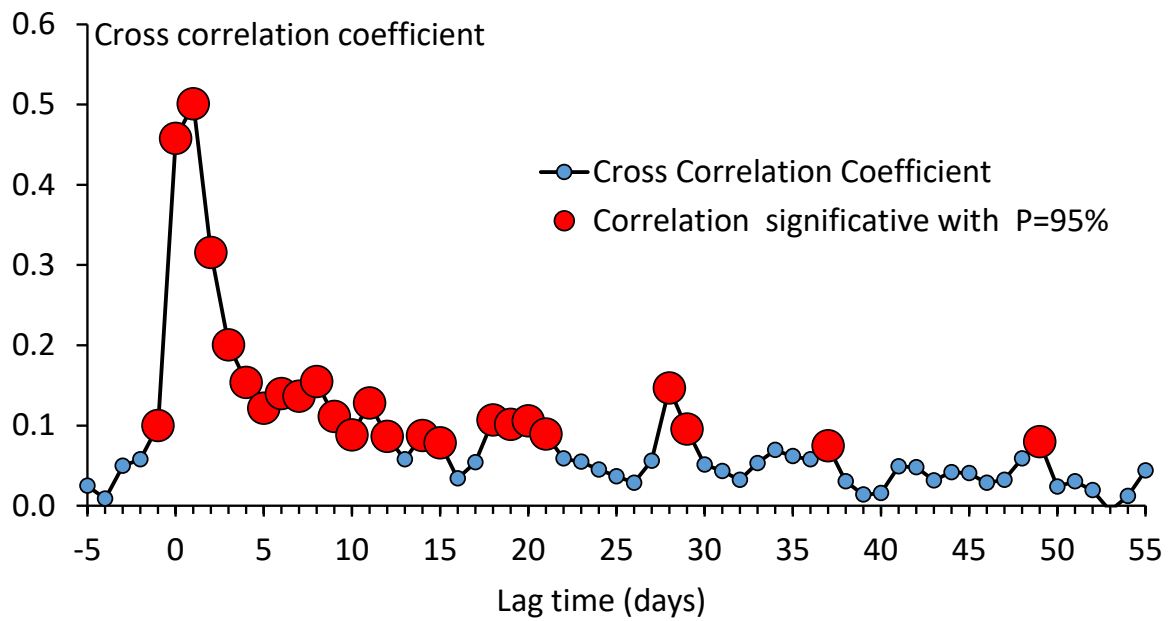
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767 **Figure 3S.** Cross-correlations between the daily precipitation (mm) and daily streamflow ($L s^{-1}$) of wadi Guenniche during the monitoring period.
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782 **Table 4S-1** : List of Ingredients quantified in water. authorized or not for agricultural use in
 783 Tunisia and/or surveyed (reported by farmers). LQ is the limit of quantification.

French analytes names	CAS N°	LQ (μL^{-1})
Analyzed. quantified. authorized. reported by farmers' surveys		
2.4-D	94-75-7	0.020
Bentazone	25057-89-0	0.020
Boscalid	188425-85-6	0.020
Carbendazime	10605-21-7	0.020
Clethodim	99129-21-2	0.050
Deltaméthrine	52918-63-5	0.020
Florasulam	145701-23-1	0.020
Glyphosate	1071-83-6	0.030
Propiconazole	60207-90-1	0.050
Simazine	122-34-9	0.020
Analyzed. quantified. authorized. Not reported by farmers' surveys		
Acetamiprid	135410-20-7	0.020
améthrine	67375-30-8	0.020
Chlorpyrifos Ethyl	2921-88-2	0.020
Chlortoluron	15545-48-9	0.020
Cyperméthrine	52315-07-8	0.020
Cyprodinil	121552-61-2	0.040
Fludioxonil	131341-86-1	0.040
Malathion	121-75-5	0.040
Métalaxyle	57837-19-1	0.020
Méthomyl	16752-77-5	0.010
Métribuzine	21087-64-9	0.010
Propamocarbe Hydrochloride (Hcl)	25606-41-1	0.020
Pyriméthanil	53112-28-0	0.040
Thiabendazole	148-79-8	0.020
Analyzed. quantified. un-authorized. reported by farmers' surveys		
Flusilazole	85509-19-9	0.050
Analyzed. quantified. un-authorized. Not reported by farmers' surveys		
AMPA (Acide Amino Méthyl Phosphonique)	1066-51-9	0.030
Anthraquinone	84-65-1	0.020
Atrazine Déisopropyl (DIA)	1007-28-9	0.020
Diuron	330-54-1	0.020
Perméthrine	52645-53-1	0.020
Piperonyl Butoxide	55218	0.040
Not analyzed. un-authorized. but reported by farmers' surveys		
Fenoxatrop	95617-09-07	-

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787 **Table4S-2:** Un-analyzed ingredients (French Names. CAS N°) authorized in Tunisia and not
788 reported by farmers' surveys.

French Analytes Names	CAS N°	French analytes Names	CAS N°
(3E.8Z.11Z) Tétradécatrien 1-Acétate	163041-94-9	Hymexazole	10004-44-1
Acétate d'ammonium	631-61-8	Iodosulfuron	185119-76-0
Alkylphénoléoxy-Ethylène		Mandipropamide	374726-62-2
Ally Isothiocyanate	57-06-7	Mefenoxam (Metalxyl)	70630-17-0
Ametoctradine	865318-97-4	Mefenpyr	135591-00-3
Aminopyralydes	150114-71-9	Meptyldinocap	131-72-6.
Amisulbrom	348635-87-0	Mesosulfuron	400852-66-6
Arylex active (halauxifen-méthyl)	943831-98-9	Metaflumizone	875656-67-0
Azadirachtine	11141-17-6	Métaldéhyde	9002-91-9
Benzovindiflupyr	1072957-71-1	Metam potassium	137-41-7
Bixafen	581809-46-3	Métam sodium	137-42-8
Capsaïcine	404-86-4	Méthoxyfénoside	161050-58-4
Chinozole (8-Hydroxyquinoline)	148-24-3	Milbemectin (A3+A4)	51596-10-2 & 51596-11-3
Chlorantraniliprole	500008-45-7	Naphoxy 2acétamide	35368-77-5
Chlormequat-chlorure	7003-89- 6	Nerolidol	40716-66-3
Chromafénozide	143807-66-3	Oxychlorure de cuivre	1332-40-7
Cloquintocet acide	88349-88-6	Phenamiphos	22224-92-6
Cyantraniliprole	736994-63-1	phenothiol	29656-15-3
Cyflufenamid	180409-60-3	Prohexadione-Calcium	127277-53-6
Cyromazine	66215-27-8	Propinèbe	12071-83-9 / 9016-72-2
Diafenthuron	80060-09-9	Proquinazid	189278-12-4
Dimoxystrobine	149961-52-4	Pyrethrins	8003-34-7
Dodine	2439-10-3	Pyridalyl	179101-81-6
Emamectin benzoate	155569-91-8	Saflufenacil	372137-35-4
Farnesol	4602-84-0	Sedaxane	874967-67-6
Fenpyrazamine	473798-59-3	S-metolachlor	87392-12-9
Flubendiamide	272451-65-7	Sodium lauryl ether sulfate	68585-34-2
Flucarbazone-sodium	181274-17-9	Spinetoram	935545-74-7
Flumetsulam	98967-40-9	Spinosade	131929-63-0
Fluopicolide	239110-15-7	Spiromesyfen	283594-90-1
Fluopyram	658066-35-4	Spirotetramat	203313-25-1
Fluoxastrobine	361377-29-9	Tepraloxymid	149979-41-9
Flupyradifurone	951659-40-8	Thiocyclame hydrogène oxalate	31895-22-4
Fluxapyroxad	907204-31-3	Triticonazole	131983-72-7
γ-Cyhalothrine	76703-62-3	Zeta-cyperméthrine	1315501-18-8
Geraniol	106-24-1	Zirame	137-30-4

791 **Table 4S-3.** Analyzed analytes. Un-detected in water samples. Un-authorized in Tunisia. not
 792 met in farmers surveys. (French Names. CAS N°. LQ is the limit of quantification)

NAME	CAS	LQ	NAME	CAS	LQ	NAME	CAS	LQ
1-(3,4-DichloroPhényl) Urée	155998	0.02	Benoxacor	98730-04-2	0.01	Chlorfenvinphos	470-90-6	0.02
DCPMU	3567-62-2	0.02	Bensulfuron-Methyl	83055-99-6	0.02	Chlorfluazuron	71422-67-8	0.01
1-(4-IsopropylPhényl) Urée	56046-17-4	0.02	Thiobencarbe	28249-77-6	0.02	Chloridazone	1698-60-8	0.05
1.2.3.4 Tétrachlorobenzène	634-66-2	0.05	β-Cyfluthrine	68359-37-5	0.02	Chlorméphos	24934-91-6	0.04
1.2.4.5 Tétrachlorobenzène	95-94-3	0.01	Bifénox	42576-02-3	0.05	Chlormequat Chloride	999-81-5	0.02
2,4' DDD	53-19-0	0.01	Bioresméthrine	28434-01-7	0.04	Chlormequat (ion)	7003-89-6	0.01
2,4' DDE	3424-82-6	0.01	Biphenyl	92-52-4	0.01	Chloroneb	2675-77-6	0.04
2,4' DDT	789-02-6	0.01	Bitertanol	55179-31-2	0.01	Chlorophacinone	3691-35-8	0.05
2,4,5-T	93-76-5	0.02	Bromacil	314-40-9	0.05	Chloroxuron	1982-47-4	0.05
2,4-DB	94-82-6	0.01	Bromadiolone	28772-56-7	0.10	Chlorsulfuron	64902-72-3	0.02
2,4-MCPA	94-74-6	0.02	Bromophos Ethyl	4824-78-6	0.04	Chlorthal Diméthyl	1861-32-1	0.01
2,4-MCPB	94-81-5	0.04	Bromophos Méthyl	2104-96-3	0.04	Chlorthiamide	1918-13-4	0.01
2,6 Dichlorobenzamide	2008-58-4	0.02	Bromopropylate	18181-80-1	0.02	Cinidon-Ethyl	142891-20-1	0.02
4,4' DDD	72-54-8	0.01	Bromoxnyl	1689-84-5	0.04	Coumaphos	56-72-4	0.05
4,4' DDE	72-55-9	0.01	Bromoxnyl Octanoate	1689-99-2	0.05	Coumatétralyl	5836-29-3	0.04
Acetochlor	34256-82-1	0.02	Buprofazine	69327-76-0	0.05	Cyanazine	21725-46-2	0.02
Acifluorfen	50594-66-6	0.04	Butraline	33629-47-9	0.04	Cyazofamide	120116-88-3	0.01
Alachlore	15972-60-8	0.04	Buturon	3766-60-7	0.05	Cycluron	2163-69-1	0.02
Aldicarbe	116-06-3	0.02	Cadusaphos	95465-99-9	0.02	Cyfluthrine	68359-37-5	0.02
Aldicarbe Sulfone	1646-88-4	0.02	Captafol	191906	0.02	Cyhalofop Butyl	122008-85-9	0.02
Aldicarbe Sulfoxyde	1646-87-3	0.02	Carbaryl	63-25-2	0.02	Dazomet	533-74-4	0.02
Aldrine	309-00-2	0.01	Carβmide	16118-49-3	0.01	DDT 44'	50-29-3	0.01
Allethrine	584-79-2	0.01	Carbofuran	1563-66-2	0.02	Déméton (O+S)	8065-48-3	0.10
Amétryne	834-12-8	0.02	Carbofuran-3-Hydroxy	16655-82-6	0.02	Demeton O	298-03-3	0.10
Amitraze	33089-61-1	0.02	Carbophénothion	786-19-6	0.04	Déméton S Methyl	919-86-8	0.10
Asulam	3337-71-1	0.10	Carbosulfan	55285-14-8	0.02	Déméton S Met. Sulf.	17040-19-6	0.10
Atrazine	1912-24-9	0.02	Carboxine	5234-68-4	0.02	IPPMU	34123-57-4	0.01
DEA	6190-65-4	0.02	Chinométhionate	196869	0.02	Diallate	2303-16-4	0.05
Azaconazol	60207-31-0	0.01	Chlorbromuron	13360-45-7	0.01	Diazinon	333-41-5	0.04
Azaméthipos	35575-96-3	0.01	Chlorbufame	1967-16-4	0.04	Dichlobenil	1194-65-6	0.05
Azimsulfuron	120162-55-2	0.05	Chlordane	57-74-9	0.01	Dichlofenthion	97-17-6	0.02
Azinphos Ethyl	2642-71-9	0.04	Chlordane α	5103-71-9	0.01	Dichlofluanide	1085-98-9	0.04
Azinphos Méthyl	86-50-0	0.04	Chlordane β	5103-74-2	0.02	Dichlofop Méthyl	51338-27-3	0.04
Bendiocarbe	22781-23-3	0.02	Chlordane γ	5566-34-7	0.02	Dichloroaniline 3,4	95-76-1	0.02
Benfluraline	1861-40-1	0.02	Chlordecyl	1034-41-9	0.01	Dichlorophène	97-23-4	0.02
Benfuracarbe	82560-54-1	0.10	Chlordécone	143-50-0	0.01	Dicofol	115-32-2	0.02
Bénomyl	17804-35-2	0.08	Chlordecyl 5b Hydro	53308-47-7	0.01	Dieldrine	60-57-1	0.01

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796 **Table 4S-4.** Analyzed analytes (Name. CAS N°. Limit of Quantification). Un-detected in
 797 water. Un-authorized in Tunisia. Not met in farmer's surveys.

NAME	CAS	LQ	NAME	CAS	LQ	NAME	CAS	LQ
Difethialone	104653-34-1	0.02	Fluridone	59756-60-4	0.05	Ioxynil Methyl Ester	3336-40-1	0.05
Diflubenzuron	35367-38-5	0.01	Flurochloridone	61213-25-0	0.04	Ioxynil Octanoate	3861-47-0	0.05
Diméfurone	34205-21-5	0.02	Flurprimidol	56425-91-3	0.02	Isazofos	42509-80-8	0.04
Dimétachlor	50563-36-5	0.05	Flutolanil	66332-96-5	0.02	Isodrine	465-73-6	0.01
Dimetilan	644-64-4	0.04	Fomesafen	72178-02-0	0.01	Isophenphos	25311-71-1	0.04
Diniconazole	76714-88-0	0.04	Fonofos	944-22-9	0.02	Isoproturon	34123-59-6	0.02
DNOC	534-52-1	0.05	Foramsulfuron	173159-57-4	0.02	Isoxaflutole	141112-29-0	0.02
Dinosèbe	88-85-7	0.04	Form. Hydrochloride	23422-53-9	0.02	Lénacile	96639	0.05
Dinoterbe	1420-07-1	0.04	Formothion	2540-82-1	0.04	MCPA-1-Butyl Ester	1713-12-8	0.05
Disulfoton	298-04-4	0.05	Fosthiazate	98886-44-3	0.02	MCPA-2-Ethyl Hex. Es.	29450-45-1	0.05
Dithianon	3347-22-6	0.05	Furalaxyl	57646-30-7	0.05	MCPA-Butoxy Et. Es.	19480-43-4	0.05
Dodemorphe	1593-77-7	0.02	Furathiocarbe	65907-30-4	0.02	MCPA-Ethyl-Ester	2698-38-6	0.05
Endosulfan α	959-98-8	0.01	HCH α	319-84-6	0.01	MCPA-Methyl-Ester	2436-73-9	0.05
Endosulfan β	33213-65-9	0.01	HCH β	319-85-7	0.01	Mecoprop (MCPP)	93-65-2	0.02
Endosulfan Sulf.	1031-07-8	0.01	HCH δ	319-86-8	0.01	Mecoprop-1-Octyl E.	161922-37-8	0.01
Endrine	72-20-8	0.01	HCH γ	1537222	0.01	Mecoprop-2.4.4-	217487-13-3	0.05
EPTC	759-94-4	0.04	Lindane	58-89-9	0.01	Mecoprop-2-but. Et. Es.	23359-62-8	0.05
Ethidimuron	30043-49-3	0.01	Hepta-Cl	76-44-8	0.01	Mecoprop-2-Et.Hex.Es.	71526-69-7	0.05
Ethion	563-12-2	0.02	Hepta-Cl- Endo Epo.	28044-83-9	0.01	Mecoprop-2-Octyl Es.	28473-03-2	0.05
Ethiophencarbe	29973-13-5	0.05	Hepta-Cl Epo. Σ iso.	28044-83-9	0.01	Mecoprop-M. Es.	2786-19-8	0.05
Fénarimol	60168-88-9	0.01	Hepta-Cl Exo Epox.	1024-57-3	0.01	Mecoprop-n/iso-but. Es.	/	0.05
Fenbuconazole	114369-43-6	0.05	Hepténophos	23560-59-0	0.02	Mefenacet	73250-68-7	0.04
Fenclorophos	299-84-3	0.05	Hexachlorobenzène	118-74-1	0.01	Mefluidide	53780-34-0	0.02
Fénitrothion	122-14-5	0.04	Hexaconazole	79983-71-4	0.05	Mepanipyrim	110235-47-7	0.02
Fenpropathrine	39515-41-8	0.02	Hexaflumuron	86479-06-3	0.04	Mepiquat Chloride	24307-26-4	0.02
Fenthion	55-38-9	0.04	Hexazinone	51235-04-2	0.05	Mepiquat (ion)	15302-91-7	0.02
Fénuron	101-42-8	0.01	Hydramethylnon	67485-29-4	0.02	Mépronil	55814-41-0	0.01
Fipronil	120068-37-3	0.01	Hydroxyatrazine	2163-68-0	0.04	Mésotrione	104206-82-8	0.01
Flazasulfuron	104040-78-0	0.10	Hydroxyterbutylazine	66753-07-9	0.02	Métamitron	41394-05-2	0.05
Flocoumafen	90035-08-8	0.02	Imazalil	35554-44-0	0.02	Methabenzthiazuron	18691-97-9	0.02
Flumioxazine	103361-09-7	0.02	Imazamétabenz-M.	81405-85-8	0.05	Méthidathion	950-37-8	0.04
Flupyrifurone M.	144740-54-5	0.10	Iodofenphos	18181-70-9	0.02	Méthoxychlor	72-43-5	0.02
Fluquinconazole	136426-54-5	0.01	Ioxynil	1689-83-4	0.04	Métobromuron	3060-89-7	0.02

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800 **Table 4S-5.** Analyzed analytes (Name. CAS N°. Limit of Quantification). Un-detected in
 801 water. Un-authorized in Tunisia. Not met in farmer's surveys.

NAME	CAS	LQ	NAME	CAS	LQ	NAME	CAS	LQ
Métoxuron	19937-59-8	0.02	Phoxime	14816-18-3	0.01	Sulcotrione	99105-77-8	0.01
Mévinphos	7786-34-7	0.04	Picloram	6607	0.04	Sulfotep	3689-24-5	0.05
Mirex	2385-85-5	0.02	Picolinafen	137641-05-5	0.02	Tébufénozide	112410-23-8	0.04
Molinate	2212-67-1	0.02	Pirimicarbe Des.	30614-22-3	0.01	Tébutame	35256-85-0	0.02
Monocrotophos	6923-22-4	0.05	Prétilachlore	51218-49-6	0.02	Teméphos	3383-96-8	0.01
Monolinuron	1746-81-2	0.02	Procymidone	32809-16-8	0.04	Terbacile	5902-51-2	0.04
Monuron	150-68-5	0.02	Profenophos	41198-08-7	0.04	Terbuméton	33693-04-8	0.02
Naled	300-76-5	0.04	Promecarbe	2631-37-0	0.01	Terbumeton Des.	30125-64-5	0.02
Napropamide	15299-99-7	0.02	Prométhryne	7287-19-6	0.05	Terbuphos	13071-79-9	0.02
Naptalam	132-66-1	0.02	Prométon	1610-18-0	0.04	Terbutryne	886-50-0	0.04
Néburon	555-37-3	0.04	Propachlor	1918-16-7	0.04	Terbutylazine Dés.	30125-63-4	0.02
Nicosulfuron	111991-09-4	0.02	Propanil	709-98-8	0.04	Tétrachlorobenzène	12408-10-5	0.05
Norflurazon	27314-13-2	0.05	Propaquizafop	111479-05-1	0.04	Tétrachlorvinphos	22248-79-9	0.04
Norflurazon Des.	23576-24-1	0.05	Propargite	2312-35-8	0.05	Tétraconazole	112281-77-3	0.05
Nuarimol	63284-71-9	0.01	Propazine	139-40-2	0.02	Tétradifon	116-29-0	0.10
Ofurace	58810-48-3	0.01	Propazine-2-Hydroxy	7374-53-0	0.02	Tétraméthrine	7696-12-0	0.04
Ométhoate	1113-02-6	0.10	Propétamphos	31218-83-4	0.04	Thiazasulfuron	25366-23-8	0.08
Oryzalin	19044-88-3	0.05	Propoxur	114-26-1	0.02	Thiodicarbe	59669-26-0	0.01
Oxadiargyl	39807-15-3	0.10	Pyrazophos	13457-18-6	0.02	Thiometon	640-15-3	0.10
Oxadiazon	19666-30-9	0.02	Pyridabène	96489-71-3	0.04	Tolclofos Methyl	57018-04-9	0.02
Oxadixyl	77732-09-3	0.02	Pyridate	55512-33-9	0.05	Tolylfluanide	731-27-1	0.04
Oxydémeton M.	301-12-2	0.02	Pyrifénos	88283-41-4	0.02	Tralométhrine	66841-25-6	0.02
Paclobutrazole	76738-62-0	0.06	Pyrimiphos Et.	23505-41-1	0.04	Triadimefon	43121-43-3	0.05
Paraquat (ion)	4685-14-7	0.01	Quinalphos	13593-03-8	0.04	Triallate	2303-17-5	0.04
Paraquat dichl.	1910-42-5	0.02	Quinoxifen	124495-18-7	0.01	Triazophos	24017-47-8	0.05
Parathion Ethyl	56-38-2	0.04	Quintozene	82-68-8	0.01	Triazoxide	72459-58-6	0.02
Parathion Méthyl	298-00-0	0.04	Rimsulfuron	122931-48-0	0.02	Triclopyr	55335-06-3	0.02
Penoxsulam	219714-96-2	0.02	Rotenone	83-79-4	0.01	Triclosan		0.10
Pentachlorobenzène	608-93-5	0.01	Sébutylazine	7286-69-3	0.02	Trinexapac Ethyl	95266-40-3	0.02
Pentachlorophénol	87-86-5	0.02	Secbuméton	26259-45-0	0.04	Vinchlozoline	50471-44-8	0.02
Phorate	298-02-2	0.04	Silthiopham	175217-20-6	0.02			
Phosalone	2310-17-0	0.04	Σ des DDT	/	0.01			
Phosphamidon	13171-21-6	0.05	Σ Endosulfan (α+β+Sulf.)	/	0.01			

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806 **Table 5S-1: Analysis methods employed CMO_MT02 and corresponding analytes.**
 807 (/ compound French name (CAS Number) /) **In red and bold** compounds detected in this
 808 study.

Method internal name "CMO_MT02"
<p>This method is used to determine pesticides, PAHs, and hydrocarbons in water intended for human consumption, including groundwater, surface water, and salt and brackish water. While the method is also applicable to wastewater, the presence of organic matter and suspended solids in such samples can cause more interferences and result in higher analytical thresholds. The method combines liquid-liquid extraction (multi-pH) with multi-detection techniques. Water samples are stored in 1L glass bottles, and extraction must be performed within 48 hours of receipt. The extraction process utilizes a separating funnel for liquid-liquid extraction. Initially, 50 mL of a dichloromethane/ethyl acetate mixture (80/20) is added to the water sample, which is then shaken for 30 minutes while ensuring degassing. The first organic phase is collected in a beaker. In the next step, 2 mL of H3PO4 and 50 mL of the dichloromethane/ethyl acetate mixture (80/20) are added to the sample and shaken for another 30 minutes. The organic phase obtained is combined with the first phase. This step is repeated, and all organic phases are mixed together. In the final step, 25 mL of dichloromethane is added, and the mixture is shaken manually. The obtained extracts are then concentrated before chromatographic analysis by LC-MS/MS or GC/MS. A high recovery rate is crucial for the fidelity and accuracy of the analytical results. The recovery rate depends on the specific compounds being analyzed and generally exceeds 60%.</p>
<p>compounds analyzed with CGMS</p> <p>1.2.3.4 Tétrachlorobenzène(634-66-2) / 1.2.4.5 Tétrachlorobenzène(95-94-3) / 2.4 D - Isopropyl-Ester(71164) / 2.4 D - Methyl-Ester(1928-38-7) / 2.4' DDD(53-19-0) / 2.4' DDE(3424-82-6) / 2.4' DDT(789-02-6) / 2.6 Dichlorobenzamide(2008-58-4) / 4.4' DDD(72-54-8) / 4.4' DDE(72-55-9) / Acetochlor(34256-82-1) / Acibenzolar-s-Méthyl(135158-54-2) / Acifluorfen(50594-66-6) / Aclonifen(74070-46-5) / Acrinathrine(101007-06-1) / Alachlore(15972-60-8) / Aldrine(309-00-2) / Allethrine(Depallethrine)(584-79-2) / Alphaméthrine(67375-30-8) / Amétryne(834-12-8) / Amitraze(33089-61-1) / Antraquinone(84-65-1) / Bénalaxyl(71626-11-4) / Benfluraline(1861-40-1) / Benfuracarbe(82560-54-1) / Benoxacor(98730-04-2) / Béta-Cyfluthrine(68359-37-5) / Bifenazate(149877-41-8) / Bifénox(42576-02-3) / Bifentrine(82657-04-3) / Bioresméthrine(28434-01-7) / Biphenyl(92-52-4) / Boscalid(188425-85-6) / Bromacil(314-40-9) / Bromophos Ethyl(4824-78-6) / Bromophos Méthyl(2104-96-3) / Bromopropylate(18181-80-1) / Bromoxynil Octanoate(1689-99-2) / Bromuconazole(116255-48-2) / Bupirimate(41483-43-6) / Buprofézine(69327-76-0) / Butraline(33629-47-9) / Cadusaphos(95465-99-9) / Captafol(191906) / Captane(133-06-2) / Carbophénouthion(786-19-6) / Carbosulfan(55285-14-8) / Carfentrazone-Ethyl(128639-02-1) / Chinométhionate(196869) / Chlorbufame(1967-16-4) / Chlordane(57-74-9) / Chlordane alpha(5103-71-9) / Chlordane Béta(5103-74-2) / Chlordane gamma(5566-34-7) / Chlorfenvinphos(470-90-6) / Chlorméphos(24934-91-6) / Chloroneb(2675-77-6) / Chlorothalonil(1897-45-6) / Chlorpropham(101-21-3) / Chlorpyrifos Ethyl(2921-88-2) / Chlorpyrifos Méthyl(5598-13-0) / Chlorthal Diméthyl(1861-32-1) / Clodinafop-Propargyl(105512-06-9) / Clomazone(81777-89-1) / Cloquintocet Methyl(99607-70-2) / Coumaphos(56-72-4) / Cycluron(2163-69-1) / Cyfluthrine(68359-37-5) / Cyhalofop Butyl(122008-85-9) / Cyperméthrine(52315-07-8) / Cyprodinil(121552-61-2) / Dazomet(533-74-4) / DDT 44'(50-29-3) / Deltaméthrine(52918-63-5) / Déméton(O+S)(8065-48-3) / Demeton O(298-03-3) / Déméton S Methyl(919-86-8) / Déméton S Methyl Sulfone(17040-19-6) / Desmétryne(1014-69-3) / Diallylate(2303-16-4) / Diazinon(333-41-5) / Dichlobenil(1194-65-6) / Dichlofenthion(97-17-6) / Dichlofluamide(1085-98-9) / Dichlofop Méthyl(51338-27-3) / Dichloroaniline 3.4(95-76-1) / Dichlorvos(62-73-7) / Dicofo(115-32-2) / Dieldrine(60-57-1) / Diflufénicanil(83164-33-4) / Diméfuron(34205-21-5) / Diméthachlor(50563-36-5) / Diméthoate(60-51-5) / Dinocap(39300-45-3) / Disulfoton(298-04-4) / Dodemorphe(1593-77-7) / Endosulfan Alpha (959-98-8) / Endosulfan Béta(33213-65-9) / Endosulfan Sulfate(1031-07-8) / Endrine(72-20-8) / EPTC(759-94-4) / Esfenvalérate(66230-04-4) / Ethion(Diethion)(563-12-2) / Ethofumésate(26225-79-6) / Ethoprophos(13194-48-4) / Etofenprox(80844-07-1) / Etoxazole(153233-91-1) / Famoxadone(131807-57-3) / Fénamidone(161326-34-7) / Fénazaquin(120928-09-8) / Fenchlorphos(299-84-3) / Fenhéxamide(126833-17-8) / Fénitrothion(122-14-5) / Fénoxaprop Ethyl(66441-23-4) / Fenpropathrine(39515-41-8) / Fenpropidine(67306-00-7) / Fenpropimorph(67306-03-0) / Fenthion(55-38-9) / Fipronil(120068-37-3) / Fluzifop-p-Butyl(79241-46-6) / Fludioxonil(131341-86-1) / Flumioxazine(103361-09-7) / Flurochloridone(61213-25-0) / Fluroxypyr Methyl Heptyl Ester(81406-37-3) / Flurprimidol(56425-91-3) / Flutolanil(66332-96-5) / Flutriafol(76674-21-0) / Folpel(133-07-3) / Fonofos(944-22-9) / Formothion(2540-82-1) / Furalaxyl(57646-30-7) / Furathiocarbe(65907-30-4) / HCH Alpha(319-84-6) / HCH Beta(319-85-7) / HCH Delta(319-86-8) / HCH Epsilon(1537222) / HCH Gamma(Lindane)(58-89-9) / Heptachlore(76-44-8) / Heptachlore Endo Epoxyde(28044-83-9) / Heptachlore Exo Epoxyde(1024-57-3) / Hepténophos(23560-59-0) / Hexachlorobenzène(118-74-1) / Imazamétabenz-Méthyl(81405-85-8) / Indoxacarbe(173584-44-6) / Iodofenphos(18181-70-9) / Ioxynil Methyl Ester(3336-40-1) / Ioxynil Octanoate(3861-47-0) / Iprodione(36734-19-7) / Isazofos(42509-80-8) / Isodrine(465-73-6) / Isophenphos(25311-71-1) / Isoxaflutole(141112-29-0) / Kresoxim Méthyl(143390-89-0) / Lambda Cyhalothrine(91465-08-6) / Lénacile(96639) / MCPA-1-Butyl Ester(1713-12-8) / MCPA-2-Ethyl Hexyl Ester(29450-45-1) / MCPA-Butoxy Ethyl Ester(19480-43-4) / MCPA-Ethyl-Ester(2698-38-6) / MCPA-Methyl-Ester(2436-73-9) / Mecoprop-1-Octyl Ester(161922-37-8) / Mecoprop-2.4.4-Trimethyl Pentyl Ester (217487-13-3) / Mecoprop-2-butoxy Ethyl Ester(23359-62-8) / Mecoprop-2-Ethyl Hexyl Ester(71526-69-7) / Mecoprop-2-Octyl Ester(28473-03-2) / Mecoprop-Methyl Ester(2786-19-8) / Mecoprop-n / iso-butyl ester(Melange)(/) / Mefenacet(73250-68-7) / Mefenpyr-diéthyl(135590-91-9) / Mepanipirim(110235-47-7) / Mépronil(55814-41-0) / Méthoxychlore(72-43-5) / Metrafenone(220899-03-6) / Mévinphos(7786-34-7) / Mirex(2385-85-5) / Molinate(2212-67-1) / "Monocrotophos(6923-22 / -4)" / Naled(300-76-5) / Napropamide(15299-99-7) / Naptalam(132-66-1) / Norflurazon(27314-13-2) / Norflurazon Desméthyl(23576-24-1) / Nuarimol(63284-71-9) / Oxadiargyl(39807-15-3) / Oxadiazon(19666-30-9) / Oxyfluorène(42874-03-3) / Parathion Ethyl(56-38-2) / Parathion Méthyl(298-00-0) / Pencycuron(66063-05-6) / Pendimethaline(40487-42-1) / Pentachlorobenzène(608-93-5) / Perméthrine(52645-53-1) / Phorate(298-02-2) / Phosalone(2310-17-0) / Phosmet(732-11-6) / Picloram(6607) / Picolinafen(137641-05-5) / Picoxystrobine(117428-22-5) / paraben / Prétilachlore(51218-49-6) / Procymidone(32809-16-8) / Profenophos(41198-08-7) / Prométhryne(7287-19-6) / Prométon(1610-18-0) / Propachlor(1918-16-7) / Propanil(709-98-8) / Propaquizafop(111479-05-1) / Propargite(2312-35-8) / Propétamphos(31218-83-4) / Proslufocarbe(52888-80-9) / Pyraclostrobine(175013-18-0) / Pyridabène(96489-71-3) / Pyridate(55512-33-9) / Pyrimiphos Ethyl(23505-41-1) / Pyrimiphos Méthyl(29232-93-7) / Piryproxyfen(95737-68-1) / Quinoxifen(124495-18-7) / Quintozene(82-68-8) / Secbuméton(26259-45-0) / Silthiopham(175217-20-6) / Sulfotep(3689-24-5) / Tau-Fluvalinate(102851-06-9) / Tébufenpyrad(119168-77-3) / Tébutame(35256-85-0) / Terbacile(5902-51-2) / Terbuphos(13071-79-9) / Terbutryne(886-50-0) / Tétrachlorobenzène(12408-10-5) / Tétrachlorovinphos(22248-79-9) / Tétradifon(116-29-0) / Tétraméthrine(7696-12-0) / Thiaflumide(Flufenacet)(142459-58-3) / Thiametoxam(153719-23-4) / Thifensulfuron Méthyl(79277-27-3) / Thiometon(640-15-3) / Tolclofos Methyl(57018-04-9) / Tolyfluanide(731-27-1) / Tralométhrine(66841-25-6) / Triadimenol(55219-65-3) / Triallate(2303-17-5) / Triazophos(24017-47-8) / Triclosan(5-Chloro-2-Phenol)(vide) / Trifloxystrobine(141517-21-7) / Trifluraline(1582-09-8) / Vinchlozoline(50471-44-8) / Zoxamide(156052-68-5) /</p>

compounds analyzed with HPLCMS

1-(3,4-DichloroPhényl) Urée(155998) / 2.4.5-T(93-76-5) / **2.4-D(94-75-7)** / 2.4-DB(94-82-6) / 2.4-MCPA(94-74-6) / 2.4-MCPB(94-81-5) / Abamectine(71751-41-2) / **Acetamiprid(135410-20-7)** / Amidosulfuron(120923-37-7) / Asulam(3337-71-1) / Azaconazol(60207-31-0) / Azaméthipos(35575-96-3) / Azimsulfuron(120162-55-2) / Azinphos Ethyl(2642-71-9) / Azinphos Méthyl(86-50-0) / Azoxystrobin(131860-33-8) / Bendiocarbe(22781-23-3) / Bénomyl(17804-35-2) / Bensulfuron-Méthyl(83055-99-6) / **Bentazone(25057-89-0)** / Benthioicarbe(Thiobencarbe)(28249-77-6) / Bitertanol(55179-31-2) / Brodifacoum(56073-10-0) / Bromadiolone(28772-56-7) / Bromoxynil(1689-84-5) / Buturon(3766-60-7) / Carbétamide(16118-49-3) / Chlorbromuron(13360-45-7) / Chlordecol(1034-41-9) / Chlordécone(143-50-0) / Chlordecone 5b Hydro(53308-47-7) / Chlorfluazuron(71422-67-8) / Chloridazone(Pyrazon)(1698-60-8) / Chlorophacinone(3691-35-8) / Chloroxuron(1982-47-4) / Chlorsulfuron(64902-72-3) / Chlorthiamide(1918-13-4) / Cinidon-Ethyl(142891-20-1) / Clofentézine(74115-24-5) / Clopyralide(1702-17-6) / Coumatétraly(5836-29-3) / Cyazofamide(120116-88-3) / Cymoxanil(57966-95-7) / Cyproconazol(94361-06-5) / Desmedipham(13684-56-5) / Desméthylisoproturon(IPPNU)(34123-57-4) / Dicamba(1918-00-9) / Dichlorophène(97-23-4) / Dichlorprop(2.4 DP)(120-36-5) / Diethofencarbe(87130-20-9) / Difenacoum(56073-07-5) / Difénoconazole(119446-68-3) / Diféthialone(104653-34-1) / Diflubenzuron(35367-38-5) / Diméthénamide(87674-68-8) / Diméthomorphe(110488-70-5) / Dimétilan(644-64-4) / Diniconazole(76714-88-0) / DiNitroOrthoCrésol(DNOC)(534-52-1) / Dinosebe(88-85-7) / Dinoterbe(1420-07-1) / Dithianon(3347-22-6) / Epoxyconazole(133855-98-8) / Ethidimuron(30043-49-3) / Ethiothencarbe(29973-13-5) / Fénarimol(60168-88-9) / Fenbuconazole(114369-43-6) / Fénoycarbe(72490-01-8) / Fenpyroximate E(134098-61-6) / Fénuron(101-42-8) / Flazasulfuron(104040-78-0) / Flocoumafen(90035-08-8) / Fluazinam(79622-59-6) / Flufénoxuron(101463-69-8) / Flupyrsulfuron Méthyl(144740-54-5) / Fluquinconazole(136426-54-5) / Fluridone(59756-60-4) / Fluroxypyr(69377-81-7) / Flurtamone(96525-23-4) / **Flusilazole(85509-19-9)** / Fomesafen(72178-02-0) / Foramsulfuron(173159-57-4) / Fosthiazate(98886-44-3) / Haloxyfop(69806-34-4) / Hexaconazole(79983-71-4) / Hexaflumuron(86479-06-3) / Hexazinone(51235-04-2) / Hexythiazox(78587-05-0) / Imazailil(35554-44-0) / Imidaclopride(138261-41-3) / Iodosulfuron Méthyl(144550-36-7) / Ioxynil(1689-83-4) / Iprovalicarbe(140923-17-7) / Isoxaben(82558-50-7) / Lufénuron(103055-07-8) / **Malathion(121-75-5)** / Mecoprop(MCPP)(93-65-2) / Mefluidide(53780-34-0) / Mésosulfuron Méthyl(208465-21-8) / Mésotrione(104206-82-8) / **Métalaxyle(57837-19-1)** / Metaldéhyde(108-62-3) / Métamitron(41394-05-2) / Métazachlore(67129-08-2) / Metconazole(125116-23-6) / Méthidathion(950-37-8) / Métolachlore(R+S)(51218-45-2) / Métosulam(139528-85-1) / **Métribuzine(21087-64-9)** / Metsulfuron méthyl(74223-64-6) / Monuron(150-68-5) / Myclobutanyl(88671-89-0) / Néburon(555-37-3) / Ofurace(58810-48-3) / Oryzalin(19044-88-3) / Oxadixyl(77732-09-3) / Oxamyl(23135-22-0) / Paclobutrazole(76738-62-0) / Penconazole(66246-88-6) / Pentachlorophénol(87-86-5) / Phenmediphame(13684-63-4) / Phosphamidon(13171-21-6) / Phoxime(14816-18-3) / Pirimicarbe(23103-98-2) / Pirimicarbe Desméthyl(30614-22-3) / Prochloraze(67747-09-5) / Promecarbe(2631-37-0) / **Propiconazole(60207-90-1)** / Propoxycarbazone Sodium(181274-15-7) / Propyzamide(23950-58-5) / Pyrazophos(13457-18-6) / Pyrifénox(88283-41-4) / **Pyriméthanil(53112-28-0)** / Quinalphos(13593-03-8) / Quinmerac(90717-03-6) / Quizalofop(76578-12-6) / Quizalofop Ethyl(76578-14-8) / Rotenone(83-79-4) / Sébuthylazine(7286-69-3) / Spinosad(168316-95-8) / Sulcotrione(99105-77-8) / **Tébuconazole(107534-96-3)** / Tébufénozide(112410-23-8) / Téflubenzuron(83121-18-0) / Teméphos(3383-96-8) / Terbutylazine (5915-41-3) / Tétraconazole(112281-77-3) / **Thiabendazole(148-79-8)** / Thiaclopride(111988-49-9) / Thiazasulfuron(25366-23-8) / Thiodicarbe(59669-26-0) / Triadimefon(43121-43-3) / Triasulfuron(82097-50-5) / Triazoxide(72459-58-6) / Triclopyr(55335-06-3) / Triflumuron(64628-44-0) / Trinexapac Ethyl(95266-40-3) /

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810 **Table 5S-2 : Analysis methods CMO_MT14 and corresponding analytes.** (/ compound
811 French name (CAS Number) /) **In red and bold** compounds detected in this study.

CMO_MT14 / HPLCMSMS

This method was developed for the determination of glyphosate, its metabolite aminomethylphosphonic acid (AMPA), and glufosinate in drinking and natural waters. The analytical approach involves derivatizing glyphosate, AMPA, and glufosinate with 9-fluorenylmethylchloroformate (FMOC-Cl) in a basic medium, followed by direct injection analysis using liquid chromatography coupled with fluorimetric detection or tandem mass spectrometry. The dissolved fractions of the three compounds are analyzed in decanted samples. Quantification is achieved either by mass spectrometry using three labeled internal standards or by fluorescence with dosed additions and an internal standard. The recovery rate generally exceeds 60%.

For detecting glyphosate, AMPA, and glufosinate using HPLC with fluorimetric detection, an Agilent 1200 series system is utilized. This system includes a gradient pump with a degasser, a refrigerated autosampler, a fluorometer, and a column heater.

Analytical Conditions: Column: Varian NH2, 5 µm, 250 x 4.6 mm (polar). Mobile Phase: Acetonitrile (ACN) + water + 0.15% H3PO4 Flow Rate: 1.2 mL/min, 77% ACN, 23% acidified water. Injection Volume: 100 µL. Wavelengths: Excitation at 260 nm, Emission at 310 nm

Results are interpreted using ChemStation software.

LCMS and/or Agilent 1200 series system

AMPA (Acide Amino Méthyl Phosphonique) (1066-51-9) / Glufosinate(77182-82-2) / Glyphosate(1071-83-6)

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Table 5S-3 : Analysis methods CMO_MT19. and corresponding analytes. (/ compound French name (CAS Number) /) **In red and bold** compounds detected in this study.

<p>CMO_MT19 / HPLCMS technique pos on line On-line solid-phase extraction (SPE) coupled with LC-MS/MS samples. PLRP-sSPE cartridges were employed for sample pre-concentration. with methanol used for backflush elution. Sensitive transitions and mass spectrometry conditions were optimized through direct infusion of individual standard solutions in positive electrospray mode. To mitigate matrix effects. water samples were spiked with internal standards</p>
<p>1-(3,4-DichloroPhényl)-3-MéthylUrée(DCPMU)(3567-62-2) / 1-(4-IsopropylPhényl) Urée(56046-17-4) / Aldicarbe(116-06-3) / Aldicarbe Sulfone(1646-88-4) / Aldicarbe Sulfoxyde(1646-87-3) / Atrazine(1912-24-9) / Atrazine Déisopropyl(DIA)(1007-28-9) / Atrazine Déséthyl(DEA)(6190-65-4) / Carbaryl(63-25-2) / Carbendazime(10605-21-7) / Carbofuran(1563-66-2) / Carbofuran-3-Hydroxy(16655-82-6) / Carboxine(5234-68-4) / Chlortoluron(15545-48-9) / Clethodim(99129-21-2) / Cyanazine(21725-46-2) / Cycloxydime(101205-02-1) / Diuron(330-54-1) / Florasulam(145701-23-1) / Formétanate Hydrochloride(23422-53-9) / Hydraméthylnon(67485-29-4) / Hydroxyatrazine(2 Hydroxy)(2163-68-0) / Hydroxyterbutylazine(66753-07-9) / Isoproturon(34123-59-6) / Linuron(330-55-2) / Mercaptodiméthur(2032-65-7) / Methabenzthiazuron(18691-97-9) / Méthomyl(16752-77-5) / Métobromuron(3060-89-7) / Métoxuron(19937-59-8) / Monolinuron(1746-81-2) / Nicosulfuron(111991-09-4) / Ométhoate(1113-02-6) / Oxydémeton Méthyl(301-12-2) / Penoxsulam(219714-96-2) / Propamocarbe Hydrochloride(Hcl)(25606-41-1) / Propazine(139-40-2) / Propazine-2-Hydroxy(7374-53-0) / Propoxur(114-26-1) / Prosulfuron(94125-34-5) / Pymetrozine(123312-89-0) / Rimsulfuron(122931-48-0) / Simazine(122-34-9) / Spiroxamine(118134-30-8) / Sulfosulfuron(141776-32-1) / Terbuméton(33693-04-8) / Terbumeton Desethyl(30125-64-5) / Terbutylazine Déséthyl (30125-63-4) / Thiophanate Méthyl(23564-05-8) /</p>

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Table 5S-4 : Analysis methods employed CMO_MT29. CMO_MT73.CMO_MT77. and corresponding analytes. (/ compound French name (CAS Number) /) **In red and bold** compounds detected in this study.

<p>CMO_MT29 / HPLCMS pour foséthyl aluminium Fosetyl Aluminium(39148-24-8)</p>
<p>CMO_MT73 / HPLCMS Shimadzu Imazamox(114311-32-9)</p>
<p>CMO_MT77 / HPLCMS Shimadzu This method allows for the determination of the concentration in drinking water, groundwater, and surface water. For wastewater, the determination is carried out for amitrole only. The analysis is performed on decanted samples. The calibration range extends from 10 to 1000 ng/L. The limit of quantification (LQ) has been validated at 20 ng/L for the four quaternary ammonium compounds (salt form) and 50 ng/L for amitrole in freshwater. These parameters have been validated according to the T90-210 standard. For wastewater (non-Cofrac), the LQ varies from 50 to 200 ng/L (amitrole only). Decanted samples are directly injected, and the quantification is performed using high-performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). Quantification is carried out using internal calibration. Each molecule has its own labeled internal standard (isotopic dilution method). The use of mass spectrometry detection in MRM (Multiple Reaction Monitoring) mode ensures the specificity of the method. A systematic 8-point calibration is performed for each analytical sequence. This calibration follows the same protocol as the samples. Use only brown polyethylene containers to prevent certain molecules (Diquat and Paraquat) from adhering to glass and to protect samples and references from UV light. Products and Reagents : Acetonitrile ULC/MS grade. Biosolve. Ammonium formate ULC/MS grade. Biosolve. Water ULC/MS grade. Biosolve. Formic acid (purity >95%)</p>
<p>Aminotriazole(61-82-5) / Chlormequat Chloride(999-81-5) / Chlormequat(ion)(7003-89-6) / Diquat(ion)(2764-72-9) / Diquat Dibromide(85-00-7) / Mepiquat Chloride(24307-26-4) / Mepiquat(ion)(15302-91-7) / Paraquat(ion)(4685-14-7) / Paraquat dichloride(1910-42-5) /</p>

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824 **Table 6S** : Active ingredients and metabolites quantified, provisional estimated yaerly loads
825 seasonal dispatch and contents in particular samples. (H =herbicide, M=Metabolite;F=
826 Fungicide,I=Insecticide)

Active Ingredients and metabolites detected	Use	Wadi Guenniche					Seasonal dispatch				Particular samples		
		Detections	Mean of contents or (single detection)	Stand ar d deviat ion	Estimated average yearly load	Estimated average yearly load	Winter (D-J-F)	Spring (M-A-M)	Summer (J-J-A)	Autumn (S-O-N)	City (El Alia) waste water	Oued Helia	19 June 2020
AMPA	H	17	3,768	±1,31	12,665	24	47	13	12	0,610	76,700	5,53	
Glyphosate	H	16	0,844	±0,13	2,568	37	24	13	28	0,580	0,490	0,86	
Simazine	M	16	0,155	±0,05	0,627	56	18	6	27	0,146	<0,02	0,26	
2,4-D	H	12	0,855	±0,79	1,688	80	4	1	27	<0,02	<0,02	0,07	
Deisopropylatrazine	M	8	0,092	±0,02	0,096	12	49	23	10	<0,02	<0,02	0,17	
Propamocarb	F	6	0,033	±0,01	>0,023	33	24	17	29	<0,02	<0,02	<0,02	
Carbendazim	F	7	0,039	±0,01	>0,029	20	28	31	19	<0,02	<0,02	<0,02	
Acetamiprid	I	2	0,165	±0,12	>0,038	3	44	41	2	<0,02	<0,02	<0,02	
Metalaxyl	F	3	0,033	±0,01	>0,018	47	28	4	26	<0,02	<0,02	<0,02	
Boscalid	F	2	0,035	0,015	>0,019	27	55	2	14	<0,02	0,236	0,05	
Permethrin	I	2	0,073	0,053	>0,029		*			1,340	<0,02	<0,02	
Diuron	H	2	0,040	0,010	>0,013	*			*	<0,02	<0,02	<0,02	
Clethodim	H	3	0,140	0,040	>0,054	*			*	<0,05	<0,05	<0,05	
Piperonyl Butoxide	I	2	0,065	0,025	>0,019			*	*	<0,04	<0,04	<0,04	
Methyl Paraben	F	2	0,078	0,014	>0,028			*	*	<0,02	<0,02	<0,02	
Chlortoluron	H	2	0,070	0,050	>0,058	*			*	<0,02	<0,02	<0,02	
Pyrimethanil	F	1	0,050		>0,009		*			<0,04	0,060	<0,04	
Chlorpyrifos	I	1	0,020		>0,017	*				0,080	<0,01	<0,01	
Cyprodinil	F	1	0,020		>0,011	*				<0,01	0,030	<0,01	
Fludioxonil	F	1	0,950		0,181		*			<0,01	0,061	<0,01	
Thiabendazole	F	1	0,020		>0,004		*			<0,02	<0,02	0,02	
Florasulam	H	1	0,110		>0,002	*				<0,02	<0,02	<0,02	
Methomyl	I	2	0,100	0,050	>0,015			*		<0,01	<0,01	<0,01	
Propiconazole	F	1	0,050		>0,011	*				<0,05	<0,05	<0,05	
Flusilazole	F	1	0,100		>0,017		*			<0,05	<0,05	<0,05	
Alphamethrin	I	1	0,182		>0,046		*			<0,05	<0,05	<0,05	
Bentazone	H	1	0,020		>0,009	*				<0,02	<0,02	<0,02	
Malathion	I	1	0,035		>0,005		*			<0,01	<0,01	<0,01	
Metribuzin	H	1	0,350		0,189	*				<0,01	<0,01	<0,01	
Antraquinone	I	0	0,019							0,019	<0,01	<0,01	
Cypermethrin	I	1	0,072							0,072	<0,05	<0,05	
Deltamethrin	I	1	0,130							0,130	<0,02	<0,02	
Total		116	8,71		18,49	12	12	5	4	2,977	77,577	6,96	

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828 **Table 7S** : Time arrangement of detected ingredients in the wadi waters using seriation^[18].

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Seasons =>	Sum.	Aut.	Win	Spr.	Sum.	Au	Win.	Spr.										
Ingredients	17-Jul-19	30-Aug-19	2-Oct-19	6-Nov-19	5-Dec-19	9-Jan-20	18-Feb-20	19-May-20	19-Jun-20	10-Jul-20	17-Sep-20	31-Oct-20	5-Dec-20	29-Jan-21	8-Mar-21	9-Apr-21	31-May-21	
Nb of detections =	9	7	10	5	9	6	6	11	7	8	6	6	4	6	10	8	10	
Methomyl																		Exclusively Beginning of period
Clethodim																		
Carbendazim																		
Florasulam																		
Propamocarb																		
Acetamiprid																		
DIA																		
Propiconazole											--NA--							Distributed along all monitoring period
Pyrimethanil																		
Flusilazole											NA							
Diuron																		
Metalaxyl											--NA--							
Glyphosate																		
AMPA																		
Thiabendazole																		
2,4-D																		
Simazin																		
Boscalid																		
Piperonyl Butoxid																		Exclusively end of period
Methyl Paraben											--NA--							
Cyprodinil																		
Metribuzin																		
Bentazone																		
Chlortoluron																		
Antraquinone																		
Cypermethrine																		
Chlorpyrifos																		
Fludioxonil																		
α-methrin																		
Tebuconazole																		
Permethrin																		
Malathion																		

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833 **Table 8S:** Analytical results (in µg/L) for detected analytes. The 17 first columns are samples from wadi Guenniche. The 3 last columns stand for: 1) City
834 waste water sample. 2) wadi El Helia. and 3) Well water.

Sampling Dates	17-Jul-19	30-Aug-19	2-Oct-19	6-Nov-19	5-Dec-19	9-Jan-20	18-Feb-20	19-May-20	19-Jun-20	10-Jul-20	17-Sep-20	31-Oct-20	5-Dec-20	29-Jan-21	8-Mar-21	9-Apr-21	31-May-21	31-May-21	31May-21	2-Oct-19
AMPA	1.95	0.74	1.56	0.47	2.14	0.69	0.47	3.38	5.53	6.19	2.43	1.81	0.76	2.86	2.69	7.08	23.30	0.61	76.70	< LQ
Glyphosate	2.23	0.42	0.29	0.39	0.26	0.87	0.21	0.52	0.86	0.86	0.82	1.42	< QL	1.36	1.05	1.00	0.95	0.58	0.49	< LQ
Simazin	0.32	0.06	0.08	< QL	0.14	0.14	0.05	0.07	0.26	0.17	0.02	0.03	0.03	0.82	0.03	0.14	0.13	0.15	< LQ	< LQ
2.4-D	0.07	0.04	0.03	< QL	9.52	< QL	0.08	0.04	0.07	0.04	0.04	< QL	< QL	< 0.08	0.09	0.17	0.07	< 0.08	< LQ	< LQ
DIA	0.17	< QL	0.11	0.03	< QL	0.06	< QL	0.05	0.17	0.13	0.02	x	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ
Propamocarbe HCl	< QL	< QL	0.07	0.02	0.02	0.02	< QL	0.04	< QL	0.03	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	0.05
Carbendazim	0.05	0.03	0.04	0.02	0.03	< QL	< QL	0.04	< QL	0.06	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Acetamiprid	0.28	0.05	< 0.02	< QL	< 0.02	< QL	< QL	< 0.02	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< 0.08	< LQ	< LQ	< LQ
Métalaxyle	< QL	< QL	0.03	< QL	< QL	< QL	0.05	< QL	< QL	< QL	x	x	< QL	< QL	< QL	0.02	< QL	< LQ	< LQ	< LQ
Boscalid	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.02	0.05	< QL	< QL	< QL	< QL	< QL	< 0.05	< QL	< QL	< LQ	0.24	< LQ
Permethrin	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.02	0.13	1.34	< LQ	< LQ
Diuron	< QL	< QL	< QL	< QL	0.05	< QL	< QL	< QL	< QL	< QL	< QL	0.03	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Clethodim	0.10	< QL	0.10	< QL	< QL	0.22	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Piperonyl Butoxide	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.04	< QL	0.09	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Methyl Paraben	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.09	0.06	x	x	x	x	x	x	x	x
Chlortoluron	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.12	0.02	< QL	< QL	< LQ	< LQ	< LQ
Pyrimethanil	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.05	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	0.06	< LQ
Chlorpyrifos Ethyl	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< 0.01	< QL	0.02	0.08	< LQ	< LQ
Cyprodinil	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.02	< QL	< QL	< QL	< QL	< LQ	0.03	< LQ
Fludioxonil	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< 0.01	< QL	0.95	< LQ	0.06	< LQ
Thiabendazole	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.02	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Florasulam	< QL	< QL	< QL	< QL	0.11	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Methomyl	0.05	0.15	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Propiconazole	< QL	< QL	< QL	< QL	< QL	< QL	0.05	< QL	< QL	< QL	x	x	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Flusilazole	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.10	< QL	< QL	x	< QL	< QL	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Alphamethrin	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.18	< QL	< LQ	< LQ	< LQ
Bentazone	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.02	< QL	< QL	< QL	< LQ	< LQ	< LQ
Malathion	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.04	< LQ	< LQ	< LQ
Metribuzin	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.35	< QL	< QL	< QL	< QL	< LQ	< LQ	< LQ
Antraquinone	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< 0.01	< QL	< QL	0.02	< LQ	< LQ
Cypermethrine	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< 0.05	< QL	< QL	0.07	< LQ	< LQ
Deltamethrine	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	0.13	< LQ	< LQ
Tebuconazole	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	< QL	x	< QL	< QL	< QL	< QL	< 0.24	< 0.24	< LQ	< LQ	< LQ

835 <QL => under quantification limit, D=> detected but under quantification limit, X=> Not analyzed