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1 **Direct measurement of selected soil functions**
2 **in a drained agricultural field: Methodology**
3 **development and case study in Saclay**
4 **(France)**

5
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25 **Abstract**

26 Over the last decade, many researchers around the world have realized the importance for
27 society of the many services provided by soils, and a significant body of research has been
28 devoted to estimating them using various types of proxies or relying on models. However, the
29 field has suffered so far from a complete lack of actual measurements with which to evaluate
30 available estimation methods. In this context, the key objective of the present research was to
31 obtain, for the first time, direct measurements of several services provided by soils. The
32 experimental site at which the research was carried out is an agricultural field located
33 southwest of Paris (France), which presents the unique advantage that is it artificially drained,
34 and therefore allows accurate mass balances to be computed over time for rain water,
35 nutrients, and herbicides applied to the soil. A detailed methodology is presented to extract,
36 from these data, quantitative measurements of 3 provisioning services (supply of water to
37 nearby stream, provision of food by supplying, respectively, water and nitrogen to wheat
38 crop), and 3 regulating functions (flood mitigation, and filtration of, respectively, nutrients
39 and herbicides). The results obtained with this methodology, and the relative significance of
40 the different services are discussed. In particular, it is shown that, given the industrial-type of
41 agriculture practiced at the site and its heavy reliance on fertilizers, the service related to the
42 supply of nitrogen to the crops by the soil is not marginal, accounting for 22% of the total
43 nitrogen consumption by the wheat. The availability of quantitative measures of selected soil
44 functions now paves the way for a detailed assessment of the various estimation methods
45 currently in use, and the development of improved approaches.

46 **Keywords:** soil functions, direct measures, field experiment, methodology development

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49 **1. Introduction**

50 In the last few decades, the fact that soils fulfill an array of important functions, in particular
51 for human societies, has become increasingly acknowledged by the public at large as well as
52 by decision-makers. Aside from supplying water and nutrients to crops, a role that will
53 become more and more crucial as the world's population rises to 10 billion people by the year
54 2050 (Foley et al., 2005), soils have a wide range of additional functions, e.g., providing
55 support to various types of infrastructure (road, buildings), hosting a rich stock of genetic
56 material, and serving to preserve archaeological artefacts (Blum, 1988 ; Baveye et al., 2016 ;
57 Jónsson and Davíðsdóttir, 2016)¹. Soils also store large amounts of organic matter, which if it
58 were mineralized, would result in huge quantities of CO₂ being released into the atmosphere,
59 potentially accelerating global warming. All these functions have been documented in detail
60 by soil scientists over the last half-century (see, e.g., Baveye et al., 2016, for a comprehensive
61 review). The topic now attracts yearly a steady stream of publications, and is the object of
62 frequent conferences and symposia.

63 Because of widespread contamination, as well as sealing due to urban sprawl in many
64 countries, soil resources are threatened worldwide, and it is urgent to manage them far more
65 efficiently than was the case in the past. In order to do so, it is rapidly becoming imperative to
66 be able to quantify explicitly the functions provided by soils, which would undoubtedly help
67 to take into consideration the value of soil in the context of land management and urban
68 planning. Various approaches have been explored in the past decade, and continue to be
69 investigated to achieve this quantification. By using the data contained in soil survey maps
70 and their statistical correlations with other parameters that are more arduous to evaluate (e.g.,

¹ In this text, we use consistently the notion of function, not in the sense given to this term in the ecosystem services framework, but as adopted in the soil science literature for the last 50 years. Baveye et al. (2016) show in detail how this concept, related to benefits derived from nature not only by humans but also by other living beings, is broader than the common understanding of “ecosystem service”. Furthermore, soil functions traditionally are not restricted to benefits that result directly from the intercession of organisms. For example, one of the functions of soils is their support to infrastructures (buildings, roads), for which the presence or absence of organisms is irrelevant (e.g., discussion in Baveye et al., 2018).

71 using pedotransfer functions), some researchers have attempted to predict quantitatively
72 several functions of soils. Another approach involves “indicators”, i.e., soil parameters that
73 are more or less closely linked with service levels, to reach the same objective. For instance,
74 soil hydraulic conductivity is used as an indicator to assess water and flood regulation
75 services (Adhikari and Hartemink, 2016). Finally, a number of investigators have tried to use
76 mathematical modelling to quantify soil services (e.g., Dominati et al, 2014 ; Palmer et al.,
77 2017).

78 A growing number of authors (e.g., Crossman et al., 2013; Pandeya et al., 2016 ; Baveye,
79 2017 ; Greiner et al., 2017 ; Robinson et al., 2017 ; Baveye et al., 2018, 2019 ; Schwilch et al.,
80 2018) have pointed out recently that a key problem of the research on ecosystem services is
81 currently facing, is the absence of direct measurements, and soil functions suffer from the
82 same drawback. Such measurements are essential to assess if the estimates obtained by using
83 soil maps, indicators, or modelling, are anywhere near the truth. In particular, as discussed in
84 detail by Baveye et al. (2016), one cannot rigorously determine whether a parameter is a good
85 indicator of a function without having numerical values of this function, with which to
86 correlate the indicator variable. Unfortunately, until now, the direct measurement of soil
87 functions has proven to be fraught with difficulties. Even though it may appear
88 straightforward to measure the crop yield on a specific agricultural land, it is not
89 straightforward to deduce from it the function the soil provided by making nutrients available
90 to the crop. Indeed, in order to do so, one has to account for climatic effects, the possible
91 occurrence of diseases, as well as the know-how and technological means of the farmer,
92 rendering the quantification of the service somewhat more arduous than would appear at first.
93 The same type of difficulty arises with the other functions provided by soils (Baveye et al.,
94 2016). For some of them, one could conceivably isolate a finite volume of soil (e.g., in a
95 lysimeter), which would make it possible to quantify fluxes in and out of the soil, and

96 therefore any change that may happen in the stock of soil constituents or chemical species.
97 But lysimeters, perforce, cannot be very large, leading to sizeable uncertainties when one tries
98 to upscale observations to the field or landscape scale.

99 Subsurface-drained agricultural fields offer a very advantageous alternative to lysimeters.
100 Many agricultural areas in Europe (Brown et van Beinum, 2009) and the world, prone to
101 waterlogging in many soils because of the presence of a minimally permeable layer at some
102 depth, have been artificially drained, sometimes centuries ago already, to allow intensive
103 agriculture to be practiced. Many studies related to N and herbicide leaching in drained soil
104 have been carried out (Kladivko et al., 1991; Boivin et al., 2006; Tournebize et al., 2015) by
105 measuring drain discharge rates and chemical concentrations in the drainage water. However,
106 concomitant monitoring of soil properties, and detailed mass balances in them, have seldom
107 been carried out. By isolating a portion of a tile-drained field, and systematically monitoring
108 what is applied at the surface and what leaves through the drain, one has in principle the
109 equivalent of a lysimeter, but at a much larger scale, which should facilitate the transition to
110 large land areas. So far, this possibility that is offered by drained agricultural fields to directly
111 measure a number of functions provided by soils does not appear to have been taken
112 advantage of.

113 In this general context, the key objectives of the research reported in the present article
114 were to develop methods that would allow the direct measurement of selected functions of
115 soils in tile-drained agricultural fields, and to apply these methods to a field near Paris
116 (France). The soil at the site that was selected for the research ideally meets our
117 specifications, since it developed in a 2-m thick loess deposit overlaying a clay bed whose
118 very low permeability is attested by the presence of a perched water table during a significant
119 part of the year.

120 **2. Material and methods**

121 2.1 Study area

122 The tile-drained agricultural field where the research was carried out is located on the Saclay
123 plateau, in the “Ile de France” region, southwest of Paris (Figure 1). The field is located
124 within a 80 km² peri-urban area currently undergoing urbanization in the context of the
125 development of the “Paris-Saclay Université” project, touted as France’s top research,
126 innovation and business cluster. The geological stratification of the plateau is typical of the
127 Parisian Basin. A layer of loam with a variable thickness covers a burrstone clay bed, called
128 “Argile à Meulières,” which lays atop the sand and sandstone of the “Sables de
129 Fontainebleau” formation (Nicole et al., 2003).

130 Measurements at the site took place over the crop cycle extending between the 20th of
131 October 2017 and the 12th of July 2018, on a 1.71 hectare plot subjected to agricultural
132 practices that are routinely practiced in the region. The soil was tilled on the 25th of October to
133 a depth of 30 cm with incorporation of residues of the previous year’s crop (i.e., maize straw).
134 Winter wheat (Lg Absalon) was planted the same day and was harvested on the 12th of July. N
135 fertilizer was applied as NH₄NO₃ on the 27th of February at a dose of 100.5 kg N ha⁻¹ and on
136 March 11 at a dose of 150.8 kg N ha⁻¹, resulting in a total application rate of 251.3 kg N ha⁻¹
137 over the growing season. When wheat reached the tillering stage, on the 6th of April 2018, the
138 field received an application of mesosulfuron-methyl, mefenpyr-diethyl, pinoxaden and
139 cloquintocet-mexyl, equivalent respectively to doses of 0.015, 0.045, 0.06, and 0.015 kg ha⁻¹.
140 During the previous maize growing season, on April 27, 2017, S-Metolachlor had been
141 sprayed on the field, at a dose of 1.92 kg ha⁻¹.

142 The experimental plot is equipped with an independent and individual drainage system
143 allowing to isolate with good confidence the contribution of the study area from adjacent
144 fields having different land uses. The site has subsurface drains (perforated polyethylene pipe
145 internal diameter = 4.4 cm;) at a depth of 1 m, and with a lateral 12 m spacing between

146 adjacent drains. The outlets of the drains are connected to a collector drain with a larger inner
147 diameter ($d= 15$ cm), discharging into an open drainage ditch (Figure 1).

148 A 2.5 m-deep trench was dug in May 2017 to describe and sample the different horizons
149 in the soil profile. The soil is classified as a silt loam Glossic Luvisol (IUSS Working Group
150 WRB, 2015). Its main physico-chemical characteristics are reported in Table 1.
151 Characteristics supposed to change with time in the upper horizon, like soil organic matter
152 and nitrogen, were re-analyzed at the beginning of the monitoring period (October 2017).
153 Average bulk density profiles were measured in each horizon in triplicate using 500-cm³ soil
154 cores (9 cm by 8.4-cm diameter). Field observations reveal the presence of a burrstone clay
155 layer at a depth between 1.8 and 2 m. Although water may still infiltrate through this type of
156 formation (Nicole et al. 2003), these fluxes are of little spatial extent and made less active
157 owing the drainage system. An evidence of this is the fact that the observation of a perched
158 water table, and the fact that the soil became rapidly waterlogged when the drainage outlet
159 was accidently cut. Thus, water flow below the clay formation is likely to make up a small
160 fraction of the total water balance (a few mm to a maximum of 20 mm / year) and that when
161 the soil above the clay layer becomes waterlogged, the only way for the water to leave is
162 through the subsurface drainage network during winter time, and through evapotranspiration
163 during other seasons.

164 **2.2 Field assessment of ES in the field**

165 To describe the assessment of soil ecosystem services, it is convenient to list them according
166 to the classification elaborated by the MEA (2005). Specifically, we shall consider three
167 different provisioning services, and three regulating services.

168 **2.2.1 Provisioning Services**

169 ***Water supply to nearby stream***

170 The presence of an impermeable clay bed at approximately 1.8 m depth prevents the soil at
171 the site from rendering a very common function of soils, i.e., the recharge of an underlying
172 aquifer, from which human populations can withdraw water to satisfy their daily needs. The
173 “perched” aquifer that develops above the clay layer at least for part of the year is too shallow
174 and not sufficiently permanent to be used for the extraction of water.

175 Nevertheless, a hydrological function that the soil fulfills, in connection with this perched
176 water layer and the presence of drains, is that it contributes water to an adjacent ditch, which
177 eventually connects with a nearby stream, the Bièvre river. The latter ultimately flows into the
178 Seine river, a few kilometers away. The amount of water that is associated with this drainage
179 during a period of time, t , corresponds to the sum of the drain water discharges during
180 successive time intervals, which can be expressed by the equation:

$$181 \quad Q = \frac{\sum_{i=1}^t q(t) \times (t^{i+1} - t^i)}{\text{field surface area}} \quad (1)$$

182 where Q (mm) is expressed as an equivalent water layer (hence the division by the field
183 surface area), $q(t)$ denotes the drain water flux ($\text{m}^3 \text{s}^{-1}$), and $(t^{i+1} - t^i)$ (s) corresponds to
184 individual time increments. Drain flow rates were monitored by systematically collecting the
185 effluent water at the lower part of the collector. The system collected the drainage water in a
186 manhole built upstream of where the collector discharges water into an open drainage ditch.
187 The monitoring system consisted of an automatic water sampler (Teledyne Isco’s, 3700)
188 coupled with a V-notch weir plate to monitor $q(t)$. Water subsamples of the drainage water,
189 with volumes proportional to the discharge rate were obtained for quality analysis (nitrogen
190 and pesticide content). Discharge at the V-notch weir plate was measured with a precision
191 water level sensor (PDCR 1830, GE Sensing). The discharge rate over each discrete time
192 interval was then calculated from the head level of the sensor recorded by a data logger (CR
193 1000, Campbell). This data logger controlled the sampling of drainage water. Each time 0.25

194 m³ of liquid flowed past the flow meter, the logger registered one pulse input. When a
195 predetermined number of pulses was reached, the logger sent a signal to the sampler to collect
196 one individual 100 ml sample. These individual samples, collected at equal increments of
197 flow volume, were combined into a single container (25 l) to form a composite sample,
198 representing an average of the characteristics (e.g., nitrogen content) of the drain flow over
199 the time increment considered.

200 *Provision of food by supplying water to crops*

201 Soils in agro-ecosystems provide food for human populations partly by supplying water to
202 plants and thereby enabling them to grow. In principle, in order to evaluate the quantity of
203 water supplied to plants, and subsequently transpired by them, in a given period of time,
204 measurements of stomatal conductance, and water potential of plant tissue are required
205 (Giménez et al., 2005), which represent an involved and painstaking endeavor. A different
206 approach consists of considering the mass balance of water in a given body of soil, and
207 deducing from it the amount of water associated with the growth of crops.

208 If one neglects any lateral subsurface or upward (capillarity rise) flow of water, as well as
209 any (bio)chemical reaction either taking up or producing water molecules, the corresponding
210 mass balance equation for a volume of soil to a depth of 1 m (h) associated with the depth of
211 the base of drains, and for a crop growing season period yields the following expression:

$$212 \quad ET = (SW_i - SW_f) + \sum_{i=1}^t P - \sum_{i=1}^t R - Q \quad (2)$$

213 where ET denotes evapotranspiration, SW (mm) is the product of the volumetric moisture
214 content θ_v and a depth h (mm) of the soil profile, and represents the amount of water
215 (expressed as an equivalent water height) present in the soil profile down to a depth h (mm),
216 $(SW_i - SW_f)$ is the variation of the soil water content in the soil profile between the start and
217 the end of the monitoring period, $\sum_{i=1}^t P$ and $\sum_{i=1}^t R$ are, respectively, the amount of rainfall

218 and water runoff at the soil surface during the same time. Since visual observation during the
219 entire growing season does not provide evidence of surface runoff, the latter is assumed
220 negligible in eq. (2). Q is the amount of drained water calculated from eq. (1).

221 Evapotranspiration, as quantified in eq. (2), does not involve just the amount of soil water
222 transpired by the plant, but also that evaporated at the soil surface. In the absence of detailed
223 measurements of this evaporation component, one has to rely on an approximation, using as a
224 guide experimental results obtained by others, under conditions that are not too dissimilar
225 from those occurring at the field site. These two components of the water budget are separated
226 here based on the work of Liu et al. (2002), who found that soil evaporation during the whole
227 growing period totaled 30 % of the total evapotranspiration, based on multi-year observations
228 of ET_c in the winter wheat cropping system without water deficit and using a large-scale
229 weighing lysimeter.

230 In our experiments, the volumetric moisture content θ_v was measured by taking soil
231 samples respectively on the 20th of October 2017 and the 12th of July 2018. At each sampling
232 date, three composite samples were taken in the field (10 m apart). Each composite sample
233 was made up of three discrete subsamples obtained in a 1x 1 m area and homogenized to
234 ensure that portions of the composite samples subsequently used for analysis were
235 representative of the whole samples. In total, nine soil cores were sampled down to 1m and
236 pooled into three composite samples for each depth. The cores were cut in 30 cm increments
237 down to 60 cm and in 40 cm increment from 60 cm to 1 m. Each composite sample, after
238 homogenization, was split into three parts for water, nitrogen and pesticide analysis. Soil bulk
239 density of the plough layer was measured in triplicate using 100-cm³ soil cores (2.5 cm by 5-
240 cm diameter). Each sample had its gravimetric water content measured and converted to
241 volumetric water content using the average bulk density profiles (Table 1). The amount of
242 rainfall, P , was recorded on site at a time step of 15 min. Additional daily weather data (air

243 temperature, air humidity, wind speed, and net radiation) were recorded at a meteorological
244 station located 500 m away from the field experiment.

245 *Provision of food by supplying nitrogen to crops*

246 Soils provide various nutrients to crops and, in principle, this function could be analyzed
247 separately for each nutrient, be it major or minor. In our experiment, we focused on nitrogen,
248 an essential nutrient. At the beginning of the crop growing season, a portion of the nitrogen
249 present in the soil is in mineral form, and another is associated with organic matter. During
250 the growing season, nitrogen is added to the soil through application of fertilizers, and some
251 nitrogen gets lost through drainage, or by denitrification or NH₃ volatilization at the soil
252 surface. During the span of a single growing season, one can consider that the soil nitrogen
253 taken by plants, N_{uptake} , does not come only from fertilizers but also from (i) the
254 mineralization of soil organic matter by microorganisms N_{SOM} , which makes nitrogen
255 available to crops, and (ii) from the initial stock, $N_{initial}$, of nitrogen in the soil (Therond et
256 al., 2017).

$$257 \quad N_{supply\ from\ soil\ to\ crop} = \frac{N_{SOM} + (N_{initial} - N_{final})}{N_{uptake}} \quad (3)$$

258 where, $N_{initial}$ (kg N ha⁻¹) and N_{final} (kg N ha⁻¹) denote, respectively, the nitrogen content at the
259 beginning and end of the growing monitoring period, whereas N_{uptake} denotes the amount of
260 mineral nitrogen taken up by the wheat.

261 The net N mineralization, N_{SOM} , i.e., the amount of nitrogen resulting from the
262 breakdown of organic matter by soil microorganisms during the growing season, is deduced
263 from the mass balance equation for soil nitrogen, as follows:

$$264 \quad N_{initial} + N_{SOM} + N_{fertilizer} = N_{final} + N_{uptake} + N_{leach} + N_{losses} \quad (4)$$

265 where $N_{fertilizer}$ represents the amount of fertilizer nitrogen applied during the same period,
266 N_{leach} , corresponds to the amount of inorganic N leached, and finally N_{losses} , represents
267 nitrogen losses by volatilization and denitrification following fertilizer application.

268 Each of the terms in this mass balance was estimated as follows. The difference ($N_{initial}$ -
269 N_{final}) in the soil down to the drains (at 1 m depth) was established on the basis of soil
270 samples obtained on 20 October 2017 and 12 July 2018, as described before. Mineral N was
271 extracted on fresh homogenized soil samples during one hour (50 g soil/100 mL 1 M KCl)
272 and analyzed by colorimetry using a continuous flow analyzer (Skalar, Breda, The
273 Netherlands) for N-NH₄⁺ and N-NO₃⁻. The analytical results expressed as concentrations were
274 converted to kg per ha using measured soil bulk density values (Table 1). Information on
275 fertilizer use by the person farming on the experimental site provided the value of $N_{fertilizer}$.
276 The following term, N_{uptake} , was measured by sampling the aboveground plant biomass (aerial
277 biomass and grain yields) in three 2-m² plots located 10 m away from each other. Nitrogen
278 stored within roots was considered to be equivalent to 25 % of the measured aboveground
279 plant biomass N content. The total dry matters (t ha⁻¹) of the aerial biomass and the grain
280 yields were calculated based on the moisture content of the aerial and grain subsamples. The
281 total N contents in the grains and aerial biomass (stems plus leaves) were determined by
282 elemental analysis. N_{leach} , the amount of inorganic N leached during the experiment, was
283 measured in the subsamples of the drainage water collected with the water sampling system
284 described before. Mineral nitrogen was analysed by colorimetry using a continuous flow
285 analyser (Skalar, Breda, The Netherlands) for N-NH₄⁺ and N-NO₃⁻. Finally, N_{losses} , nitrogen
286 losses by volatilization and denitrification following fertilizer application, was estimated to be
287 equal to 7.3 kg N ha⁻¹ according to literature for comparable conditions (crop type, climatic
288 conditions, fertilizer): nitrogen losses by volatilization (N-NH₃) was fixed to 1 kg N ha⁻¹
289 according to Ramanantenasoa et al. (2018); N-N₂O emission by denitrification was fixed to

290 2.5 % of the applied N according to the work of Henault et al. (1998), who measured N-NO₂
291 fluxes during 5 months following NH₄-NO₃ fertilizer application for an experimental plot
292 located on a similar soil type (hydromorphic gleyic Luvisol) and also cropped with wheat.

293 **2.2.2 Regulating services**

294 *Flood mitigation*

295 Flood mitigation in this study refers to the ecosystem's capacity to reduce the impact of
296 floods at the local scale. This service is supported by different processes such as interception
297 of rainfall, evapotranspiration, infiltration and drainage, and water storage in soil. The
298 provision of the function "flood mitigation" was assessed by (i) measuring the ability of the
299 soil to buffer rainfall under humid conditions and during extreme rainfalls, and (ii) monitoring
300 the fluctuations of the perched water table. Following Topp et al. (1997) and Reynolds et al.
301 (2003), the hydraulic conductivity near saturation was measured to evaluate the ability of the
302 soil to drain excess water out of the root zone. The hydraulic conductivity – matric potential
303 relationship was measured with a disc infiltrometer at different matric potentials from -15 cm
304 up to -1 cm, at different depths (15, 65 and 75 m) by digging a trench. Fluctuations of the
305 water table below the soil surface were monitored using a piezometer (PWS, RocTest)
306 installed at 1.8 m depth in the field. Monitoring was carried out with a time step of 15 min
307 and recorded by the data logger.

308 *Filtration of nutrients (Nitrogen)*

309 The traditional perspective on this function (e.g., Blum, 1988; Dominati et al., 2014; Baveye
310 et al., 2016) is that it corresponds to the retention by the soil of nitrogen applied at the surface
311 or produced internally. The key outcome of this process, when the function is fulfilled, is that
312 a tolerable amount of nitrogen reaches groundwater resources, or as is the case on the Saclay
313 plateau, is directly discharged into nearby streams. To quantify this function, one approach is

314 to relate the amount of nitrogen that is leached to the amount that is either applied or
 315 internally produced (Villamagna et al., 2013; Therond et al., 2017). It is defined here as the
 316 nitrogen retained in the soil, expressed as a proportion of total mineral N considered as inputs
 317 in the soil system. From that perspective, the effectiveness of the soil in supplying this service
 318 can be quantified as follow

$$319 \quad N_{filtered} (\%) = \left(1 - \frac{N_{leach}}{N_{initial} + N_{fertiliser} - N_{losses} + N_{SOM}} \right) \cdot 100 \quad (5)$$

320 In this equation, the presence of the term N_{losses} is based on the assumption that losses of
 321 nitrogen by volatilization or denitrification follow relatively after application of fertilizers to
 322 the field. The denitrification potential of the lower horizons was negligible due to the low
 323 content of soil organic carbon (D'Haene et al., 2003). Therefore the amount of nitrogen that is
 324 actually applied to the field can best be approximated by the difference $N_{fertilizer} - N_{losses}$.

325 ***Filtration of contaminants (Herbicides)***

326 In a manner similar to what was used in the case of nitrogen, the retention of herbicide by the
 327 soil was assessed by relating the amount of herbicide that is leached to the amount that is
 328 either present initially in the soil or applied to it, as follows:

$$329 \quad herbicide_{filtered} (\%) = \left(1 - \frac{herbicide_{leach}}{herbicide_{initial} + herbicide_{added}} \right) \cdot 100 \quad (6)$$

331 where, ($herbicide_{initial}$) denotes the herbicide content in the soil down to the drains (1m
 332 depth) at the beginning of the monitoring period, on the basis of soil samples obtained on 20
 333 October 2017, as described before; $herbicide_{added}$ represents the amount of herbicide
 334 applied by the farmer. The analytical results expressed as concentrations were converted to kg
 335 per ha using measured bulk density values (Table 1).

336 Two chemicals differing in their rate and application schedule were considered in this
 337 study. The first is the herbicide S-Metolachlor, applied in April 2017 at a relatively high rate

338 (1.92 kg ha⁻¹). The herbicide and its two metabolites, metolachlor-OA (oxanilic acid) and
339 metolachlor-ESA (ethane sulfonic acid), were extracted from soil samples, and were analyzed
340 in drained water samples and soil extracts following the method described by Chabauty et al.
341 (2016). The soil was first frozen, lyophilized and ground. Then, 5 g of soil were extracted by
342 sonication and concentrated by off-line SPE. The concentrations of S-Metolachlor and its
343 metabolites OA and ESA in soil extracts were determined by injecting 10 µL, by ultra-high
344 performance liquid chromatograph (Acquity UPLC, Waters) coupled through an electrospray
345 interface to a tandem mass spectrometer (TQD, Waters). The limits of quantification for S-
346 Metolachlor, OA and ESA were 0.25, 1.35 and 1.35 µg/kg in dry soil and 0.005, 0.05, and
347 0.01 µg/L in soil solutions, respectively.

348 The second herbicide consists of a mixture of two different herbicides, Mesosulfuron-
349 methyl and pinoxaden, along with the two herbicide safeners mefenpyr-diethyl and
350 cloquintocet-mexyl. This mixture was applied in April 2018, equivalent respectively to doses
351 of 0.015, 0.045, 0.06, and 0.015 kg. ha⁻¹. To estimate the pesticide fraction that actually
352 reached the soil, a field experiment was conducted during this second herbicide application.
353 Petri dishes filled with soil from the field were put above the crop foliage at three different
354 locations, to measure the total fraction that reached the upper part of foliage and the soil
355 surface. Just after chemical applications, surface soil (2 cm of thickness) below the canopy
356 was sampled to quantify the amount of herbicide that reached the soil surface. Soil sampling
357 campaigns were also held 13 days after herbicide application to measure chemical
358 concentrations. Mesosulfuron-methyl, mefenpyr-diethyl, pinoxaden and cloquintocet-mexyl
359 were extracted from soil samples, analyzed in drained water samples and soil extracts by the
360 laboratory Girpa (Beaucouzé, France). The procedure adopted for pesticide analysis in the soil
361 was based on the QuEChERS (NF EN 15662, 2009) sample preparation method. The choice
362 of the buffer, type of extract solvent, shaking time and dispersive solid phase extraction (d-

363 SPE) clean-up were optimized following Anastassiades et al. (2003). The procedure involves
364 initial single-phase extraction of 10 g sample with acetonitrile, followed by liquid–liquid
365 partitioning by addition of anhydrous MgSO₄ and NaCl. Removal of residual water and
366 cleanup are performed simultaneously by using a procedure called dispersive solid-phase
367 extraction (dispersive-SPE), in which anhydrous MgSO₄ and primary secondary amine
368 sorbent are mixed with acetonitrile extract. An aliquot of the final extract is taken for analysis
369 by LC/MS.MS. In parallel, a multi-residues analysis by GC-ECD/FPD is performed on the
370 ethyl acetate extract solvent. Quantification of the pesticide residues was carried out by liquid
371 chromatography-tandem mass spectrometry (LC-MS.MS), gas chromatography–electron-
372 capture detection (GC-ECD). The recovery rates ranged from 79% to 106%. The limit of
373 quantification was 10 µg/kg for soil extracts and 0.05 µg/L for drained water samples.

374 **2.2. 3 Uncertainty analysis**

375 The associated uncertainties in the estimates of soil functions were predicted from errors of
376 measured variables/components relative to each function using an uncertainties propagation
377 model (Taylor et al., 2017). The model predicates that if various quantities x, \dots, w are
378 measured with uncertainties $var\ x, \dots, w$ and the measured values are used to calculate some
379 quantity q , then the uncertainties in x, \dots, w cause an uncertainties in q as follows:

$$380 \quad \quad \quad var\ q = var\ x + \dots var\ w \quad \quad \quad (7)$$

381 The underlying assumption of this model is that even when there is an interrelationship
382 between various parameters, their associated uncertainties are not correlated. This condition
383 appears reasonable in this study because measurement of each component/variables is
384 independent of the measurement of the other components. Uncertainties of measurements like
385 soil bulk density, soil water content, soil nitrogen content, soil herbicide content, and nitrogen
386 uptake (Table 2) were used in the prediction of uncertainties of their associated soil functions.

387

388 3. RESULTS AND DISCUSSION

389 3.1 Provisioning Services

390 *Water supply to nearby streams*

391 Water supply to Bièvre river, nearby stream, was assessed from measurements of drain water
392 discharges during the monitoring period (Eq. 1 and Figure 2). The total volume of water that
393 drained from the field amounted to 334 mm for the whole monitoring season, from October
394 20, 2017, to July 12, 2018. The uncertainty associated with this measurement, from
395 manufacturer data, is around 3 %. The water supply to nearby streams represents 53 % of the
396 total volume of precipitations (625 mm). It compared well with the hydrological functioning
397 that was observed for similar soils of the Paris Basin (Branger et al. 2009; Tournebize et al.,
398 2015).

399 To better understand the temporal furniture of the service of water supply, the drainage
400 period was split in three key periods (Figure 2 b). During the first period, from October 18,
401 2017, to the end of December, the cumulative rainfall curve rises steadily, unlike the
402 cumulative drainage one, which takes off only after December 10, and even then at a slower
403 rate. The cumulative drainage between November 28 and December 31 corresponds to about
404 32% of the cumulative rainfall, which implies that about 68% of the rainfall does not
405 contribute to water supply during that period. A second period, which can be characterized as
406 a time of intensive drainage, extends approximately from the end of December until the 13th
407 of March 2018. During that period, the cumulative drainage curve runs roughly parallel to the
408 cumulative rainfall one, which means that 100% of the rain (equivalent to a 209 mm layer)
409 contributed to water supply. The third period of drainage (from the 13st of April onward) is
410 characterized by less frequent rainfall events, and an increase of the evaporative demand,
411 which results in a flat cumulative drainage curve for much of the time, and a continuous drop

412 of the water table, below two meters even in late early June. During this last period, only 24
413 % of the rainfall contributed to water supply. As a result, more rainfall during the time of
414 intensive drainage systematically induces an increasing water supply while it is far less the
415 case outside of the intensive drainage period.

416 As already pointed by Cornu et al., (2018) after monitoring the drainage discharge to
417 nearby stream for a three year period, the water supply cannot be determined solely by the
418 difference between total annual rainfall and evapotranspiration as it is commonly performed
419 in several of the modelling tools already classically used for ecosystem services assessment
420 and decision making (Sharps et al., 2017) but must take into account the temporal distribution
421 of precipitation. In the considered growing period, the difference between rainfall (625 mm)
422 and evapotranspiration (453 mm as calculated by the Penman-Monteith equation (Allen et al.,
423 1998), more details in the following) is equal to 170 mm. Such assessment underestimated the
424 real water supply by almost one hundred percent.

425 ***Provision of food by supplying water to wheat crop***

426 During the whole growing season, a total of 625 mm of precipitation fell on our field site.
427 According to Steduto et al. (2012), this amount of rainfall is in principle adequate for wheat to
428 grow, develop, and achieve a yield of the order of $8,5 \pm 2 \text{ t ha}^{-1}$, as was measured at our field.

429 On the basis of meteorological data measured in the field, the reference potential
430 evapotranspiration, ET_0 , was calculated by the Penman-Monteith equation (Allen et al., 1998)
431 during the growing season, and was found to be equal to 455 mm. If, following Liu et al.
432 (2002) and Steduto et al. (2012), the K_c value for the whole growth period of winter wheat is
433 set equal to 0.93, the potential evapotranspiration of wheat ($ET_C = ET_0 * K_c$) is equal to 423
434 mm. This value is similar to that of Liu et al. (2002), who observed that total water
435 consumption averaged 453 mm for a winter wheat crop in the absence of water deficit.

436 In order to calculate the actual water supply from soil to crop and atmosphere, i.e., the
437 actual evapotranspiration (ET), measurements of the different water fluxes in the hydrological
438 budget at our field site can be introduced in Eq. 2. With $SW_i - SW_f$ equal to 72 mm,
439 $\sum_{i=1}^t P$ equal to 625 mm $\sum_{i=1}^t R$ equal to 0, and Q equal to 334 mm, an ET value of 363 mm
440 of water is obtained, which is slightly less than the potential ET_C and accounts for 58 % of the
441 rainfall. In table 2, we have collected all the elements related to the uncertainty associated
442 with measurements. Using a standard error propagation formula (Eq. 7), we calculated an
443 overall uncertainty for this function, expressed as coefficient of variation, equal to 2 %. This
444 value is a lower-bound, an optimistic estimate because only uncertainties associated with
445 measurements of initial and final water content (SW_i and SW_f of Eq.2) were available and
446 included in equation to calculate an overall uncertainty for the water supply service. Based on
447 the work of Liu et al. (2002) who found transpiration equivalent to 70 % of the total ET_C , we
448 can estimate that the transpiration during the growing period in our experiment was equal to
449 254 mm.

450 The (potential) supply of water to crop is estimated through a great diversity of indicators
451 among which the water retention potential (Grimaldi et al., 2014; Calzolari et al., 2016). The
452 water retention potential of the first 100 cm of the studied soil was estimated to range from
453 153 to 200 mm depending on the pedotransfer function used (Predal A., 2018). The classical
454 estimation of the water retention potential from granulometric information available in soil
455 maps thus underestimated the real supply of water to crops by 54 to 101 mm, which is not
456 surprising as the water retention potential is regularly refilled during the crop growth. If the
457 underestimation appears limited in the considered case and the water retention potential as a
458 suitable proxy to assess the water supply function/service, this is very likely because i) the
459 soil under study received an adequate amount of rainfall (625 mm) compared to the potential
460 and actual need of the crop and atmosphere ($ET_C = 423$ and $ET = 363$ mm), ii) the entire soil

461 profile is very well and uniformly colonized by roots, iii) the high soil hydraulic conductivity
462 at saturation (with an average of 746 mm/day) is indicative of “ideal” conditions for the
463 redistribution of crop-available water (Topp et al., 1997; Reynolds et al., 2003); and finally
464 iv) the land drainage evacuated the water in excess out of the root zone. Such ‘ideal’
465 conditions are however not the rule and the water retention potential may consequently be less
466 efficient than measured here to assess the real water supply to crops.

467 ***Provision of food by supplying nitrogen to crops***

468 Mass balance calculations, as described schematically in Figure 3, allow us to determine the
469 amount of nitrogen that is directly supplied to crops by the mineralization of soil nitrogen.
470 With measured values of N_{init} (61.7 kg N ha⁻¹ on 20 October 2017), N_{final} (13.4 kg N ha⁻¹ on 12
471 July 2018), $N_{fertilizer}$ (251.3 kg N ha⁻¹), N_{uptake} (268.9 kg N ha⁻¹), N_{leach} (34.4 kg N ha⁻¹), and
472 with a literature-based estimate of N_{losses} (7.3 kg N ha⁻¹), it is possible through eq. (4) to
473 calculate N_{som} , whose value is equal to 11.1 kg N ha⁻¹.

474 The outcome of these calculations is that the total sum of the N that is directly or indirectly
475 contributed by the soil itself and potentially used by crop, i.e., the sum of the change in soil
476 mineral nitrogen content between the beginning (mainly released by mineralization of soil
477 organic matter in last summer) and the end of the experiment, and the nitrogen produced by
478 mineralization of organic matter during the experiment, was found equal to 59.4 kgN.ha⁻¹.

479 This represents 22 % of the measured crop N uptake, in line with other studies (e.g., Palmer et
480 al., 2017), which found that in agroecosystems where N was not limiting growth (i.e., when
481 fertilizer applications were sufficiently high), the nitrogen supplied to crops by fertilizer
482 application dominated the amount of N derived from mineralization of soil organic matter.

483 The standard error propagation formula calculate an overall uncertainty for this ES equal to
484 80 %, which is quite significant. Plant N uptake was the major source of this high uncertainty
485 (Table 2).

486 One might have reasonably expected the amount of nitrogen contributed by the
487 mineralization of the organic matter to be significantly larger than this number, which is very
488 small relative to the amount of nitrogen added as chemical fertilizer. This might be explained
489 to some extent by the small amount of soil organic matter present in the soil (1.6 % in the first
490 42 cm of the soil profile, Table 1), the fact that the monitoring period did not include the
491 summer season (from 12 July to the end of September), generally characterized by a high rate
492 of mineralization of organic matter, and also by the incorporation of maize straw with a high
493 C/N ratio (130) in the soil during the day of sowing wheat (Recous et al., 1995; Mary et al.,
494 1996). The mineralization of this maize straw by soil microorganisms has been shown to
495 require as much as 33 g N per kg of carbon added, in the 4 months that follow incorporation
496 of the straw in the soil (Trinsoutrot et al., 2000). In the case of our experiments, the resulting
497 N immobilization by microorganisms may amount to up to 14 kg N ha⁻¹ per ton of straw
498 incorporated, which would definitely explain why the observed net N mineralization rate in
499 the soil is so low.

500 This relatively low percentage of nitrogen directly contributed by the soil to the wheat
501 crop raises an interesting point about the service that the soil is providing to the crop. Indeed,
502 it turns out that this service is not so marginal, compared to what the fertilizer, applied by the
503 farmer, is contributing to the plants. Of course, this is a reflection of the type of industrial
504 agriculture that is practiced on the site. Were the farmer to switch to a more durable form of
505 agricultural practice, in which a significant portion of the nitrogen would be supplied by
506 legumes intercropping or by the application of organic amendment, the outcome would be
507 different.

508 **3.2 Regulating services**

509 *Flood mitigation*

510 This service, provided by the soil at our experimental site, can be apprehended locally, on the
511 site itself, or at a broader scale, downstream from the site. In terms of flooding at the site, no
512 visible signs of water accumulation at the surface or runoff were encountered in the study area
513 during our frequent site visits in 2017 and 2018, either as runoff water or as puddles in surface
514 depressions of the microtopography. This means that our ecosystem through its capacity of
515 water storage, infiltration and drainage was able to mitigate completely (100 %) floods during
516 the different period of seasons and especially during extreme rainfalls. At first glance, this
517 observation would seem consistent with the measurements that were made of the saturated
518 hydraulic conductivity at the site. This parameter, taken as an indicator of the ability of the
519 soil to drain excess water out of the root zone, was with an average of 746 mm/day and a
520 coefficient of variation equal to 58 % (Table 2) along the soil profile. According to Topp et
521 al. (1997) and Reynolds et al. (2003), this value is in general considered “ideal” to reduce
522 surface runoff and soil erosion, and rapid drainage of excess soil water. However, any attempt
523 to interpret the flood mitigation function on that basis would undoubtedly be misled. Because
524 of the presence of a clay layer at shallow depth, the soil down to that layer would have a
525 tendency to fill with water after rain events, making ponding at the surface extremely likely,
526 unless an effective drainage system were installed. Indeed, a few fields in the vicinity of our
527 experimental site, where it was clear that drains had failed and no longer conducted water to
528 nearby ditches, showed evidence of ponding or were even waterlogged for extended periods
529 of time during intensive drainage period.

530 To prevent ponding at the surface, the drainage system has to be able to evacuate water
531 fast enough so that the water table never reaches that level. Measurements of the water table
532 elevations over time (Figure 2 a) show that the water table level did not come up above 40 cm
533 below the surface, even after rainfall events of high intensities. Therefore, the drainage system
534 is working as expected, but in terms of the broader hydrological scene in the area, drainage of

535 a field cannot be too rapid. Given the size of the Saclay plateau, if in each field, drains start
536 releasing water to nearby ditches within minutes after a rainfall event, there would be a
537 sizeable risk of flooding downstream.

538 In general, it appears in Figure 2 a, b that drainage flow peaks are delayed by hours to
539 days, and are very much damped down, relative to rainfall peaks. For example, the highest
540 rainfall peak in this figure, which occurred in a very short period of time (between 4 and 12 of
541 June 2018), at a time of high evaporative demand at the soil surface, and involved 111 mm of
542 rain (an event with a return period of 50 years), caused a significant and rapid rise of the water
543 table in the soil, and led to a significantly damped peak drain flow (only 18 mm). This means
544 that soil fulfilled its aim very well by storing more than 80 % of rainfall. The only times when
545 drainage peak flows were commensurate with rainfall intensities, or even exceeded them as
546 on 22/01/2018 and 11/02/2018, were during periods where the water table was relatively high
547 and the soil above it very moist, so that, as described by Voltz et al. (2018), even a small
548 amount of rainfall could considerably raise the water table and rapidly increase the drainage
549 flux.

550 The fact that no flooding has been reported in the area during the experiment suggests
551 that perhaps the damping and delay caused by the soil at our experimental site after the
552 various rainfall events we monitored, particularly the extreme events of June, may have been
553 sufficient to minimize flooding risks. However, clearly, to fully assess the risk of flooding
554 downstream of our field site would require a detailed analysis of streamflow in the nearby
555 river over a much longer period of time than the single growing season considered here.

556 *Filtering of nutrients (Nitrogen)*

557 The filtering of nutrients at the field site, was computed according to equation (5), which
558 takes into account the initial stock of mineral N ($61.7 \text{ kg N ha}^{-1}$), N losses that may occur in
559 the system ($34.4 \text{ kg N ha}^{-1}$), as well as the amount of nitrogen mineralized from the soil

560 organic matter (11.1 kg N ha⁻¹). This calculation yields a value of $N_{filtered} = 89.1 \%$, implying
561 that 10.9% of the nitrogen that is applied to the soil or is produced internally ends up in the
562 drain. This is still a somewhat high number, and one could consider that the ability of the soil
563 to filter nitrogen is not optimal. The overall uncertainty for this function by computing errors
564 of parameters for which we have values (Table 2) was 17 % under the conditions of this
565 study.

566 The measured mineral nitrogen losses in the drained water amounted to 20.3 kg N ha⁻¹ from
567 20 October to 22 January and 14.1 kg N ha⁻¹ from 24th January to 12th of July 2018 (Figure 3).
568 Effluent data over time (Figure 4) also indicate that the quantity of mineral N in the drained
569 water (as a percentage of the total over the growing season) is highly linked to the quantity of
570 drained water that exits the experimental site. The higher amount of nitrogen lost during the
571 winter period was related to the low crop demand and high residual soil N stock. We suppose
572 also that the presence of straw maize, which immobilized a portion of the N present in the soil
573 decreased the intensity of N leaching (Beaudoin et al. 2005; Baoqing, et al. 2014). The first
574 authors observed that incorporation of straw residues led to 24 kg N ha⁻¹ reduction in N
575 leaching.

576 Again, as with the previous function, the filtering of nutrients at the field site can be
577 interpreted in different ways according to the beneficiary of the function. Another perspective,
578 which is likely to be adopted by farmers concerned about the (financial) bottom line, consists
579 of considering only the amount of nitrogen that is applied as fertilizer at the soil surface
580 during the growing season, and the amount that leaves the field site in the drain water.
581 According to this “black box” approach, 251.3 kg N ha⁻¹ are applied, and 34.4 kg N ha⁻¹ leave
582 the site, which can be interpreted to mean that a relatively sizeable 13.7 % of the fertilizer
583 applied to the field is not filtered by the soil and ends up in the nearby ditch. From an
584 economic viewpoint, these 13.7 % are a net loss, which the farmer could conceivably try to

585 reduce, for example by adapting application rate according to crop demand using precision
586 farming.

587 Yet another viewpoint that can be adopted is to determine to what extent the drain water
588 that leaves the experimental site exceeds regulatory standards. For drinking water, the World
589 Health Organisation (WHO, 2011) sets for nitrate a “guideline value”, defined as the
590 concentration of a constituent that does not result in any significant risk to health over a
591 lifetime of consumption, of 50 mg l⁻¹, which is also the threshold adopted by the European
592 Union. That concentration is exceeded from mid-December to January 20 (Figure 5).
593 However, one could consider that a more relevant range of acceptable concentrations would
594 be that found normally in nature. In that respect, according to the WHO (2011b), the nitrate
595 concentration in surface water typically ranges from 0 to 18 mg per liter. In the drain water
596 exiting our experimental site exceeded this value of 18 mg l⁻¹ from the start of the monitoring
597 in October to mid-April, i.e., during the Winter and early Spring, when the wheat crop was
598 dormant and consumed little or no nitrogen.

599 *Filtering of contaminants (Herbicides)*

600 The first type of pesticide, S-Metolachlor, was applied at a rate of 1920 g ha⁻¹ on 27 April
601 2017 before the beginning of our experiment. Analysis of S-Metolachlor within the soil
602 profile on October 20, 2017, showed a soil concentration of 26 µg/kg and 2 µg/kg in the 0-30
603 cm, 30-60 cm soil layers. S-Metolachlor concentrations were below detection limits in the soil
604 layer from 60 to 90 cm. These concentrations, converted to g per ha using the bulk density
605 values, are equivalent to 118 g.ha⁻¹ in the whole profile (Figure 6). S-Metolachlor
606 concentration in soil decreased to 77 g. ha⁻¹ within the whole soil profile at the end of
607 experiment. The cumulative amount of S-Metolachlor exported in drained water has been
608 recorded equal to 1.1 g.ha⁻¹ during the period of our experiment. From equation (6), the
609 retention of S-Metolachlor by the soil was found equal to 99.1 % by relating the amount of

610 herbicide that is leached during the monitoring period ($herbicide_{leach} = 1.1 \text{ g}\cdot\text{ha}^{-1}$) to the
611 amount observed within the soil profile on October 25, 2017 ($herbicide_{initial} = 118 \text{ g}\cdot\text{ha}^{-1}$). The
612 standard error propagation formula calculate an overall uncertainty for this ES equal to 58 %,
613 which is quite significant. S-Metolachlor concentrations in soil was the major source of this
614 uncertainty (Table 2). The retention of S-Metolachlor could not be evaluated from the date of
615 its application (April) because the amount of S-Metolachlor that is leached between April and
616 October is unknown.

617 Metolachlor-OA and Metolachlor-ESA, degradation products of S-Metolachlor, were
618 measured and monitored within the soil profile and in drained water. Metolachlor-OA
619 concentrations was equal to $10 \mu\text{g}/\text{kg}$ and $2 \mu\text{g}/\text{kg}$ in the 0-30 cm, 30-60 cm soil layers on 25th
620 of October, which is respectively equivalent to $41 \text{ g}\cdot\text{ha}^{-1}$ and $10 \text{ g}\cdot\text{ha}^{-1}$. The potential for
621 Metolachlor-OA storage in soil is limited: this metabolite is dissipated along the soil profile at
622 the end of the experiment (8 months later) (Figure 6). Metolachlor-ESA concentrations within
623 the whole soil profile were below detection limits. Drained water showed large concentration
624 differences between S-Metolachlor, and its metabolites Metolachlor-OA and Metolachlor-
625 ESA (Figure 7). The Metolachlor-ESA concentrations were observed to be between twice and
626 ten times higher than Metolachlor-OA concentrations. The two degradation products of S-
627 Metolachlor were found at concentrations exceeding drinking water guidelines for surface
628 water during the whole period (Figure 7). These results are consistent with findings in other
629 studies, which show that degradation products of S-Metolachlor are found in much higher
630 concentrations than the parent compound in groundwater and are above threshold levels set
631 by drinking water guidelines (Phillips et al., 1999, Farlin et al., 2018).

632 The parent compound, S-Metolachlor, exhibited a particular behavior during the period
633 following the high rainfall events at the beginning of June. S-Metolachlor concentrations in
634 the drained water increased 19 and 27 times, respectively, on June 18 and July 12, compared

635 to the average for the rest of time. The higher amount of this chemical lost during this period
636 could be related to the extremely high amount of rain (111m equivalent) that occurred during
637 a very short time span.

638 The cumulative amount of Metolachlor-OA and Metolachlor-EA exported in drained
639 water has been found respectively equal to 3.3 and 8.7 g.ha⁻¹. Again as with S-Metolachlor, it
640 is possible through eq. (6) to calculate the filtering of the Metolachlor-OA at the field site by
641 relating the $herbicide_{leach} = 3.3 \text{ g.ha}^{-1}$ to the amount observed within the soil profile on
642 October 20, 2017 ($herbicide_{initial} = 51 \text{ g.ha}^{-1}$). This calculation yields a value of filtered
643 Metolachlor-OA equal to 93.5 %, implying that this S-Metolachlor metabolite is less retained
644 by the soil than S-Metolachlor.

645 Concerning the evolution of the relative fluxes of these different chemicals in drained
646 water, expressed as the ratio of the total amount observed over the whole drainage season
647 (Figure 4), the two metabolites showed the same leaching potential during the drainage
648 season, in contrast to S-Metolachlor, except for the period following the high rainfall events
649 in June . This suggests that S-Metolachlor's metabolites were formed in the soil and were
650 much more mobile than S-Metolachlor. This is also consistent with their smaller adsorption
651 coefficients (koc ESA= 5-20 l/kg, Koc 5-20 l/kg for OA) compared to the value found for S-
652 Metolachlor (Koc =114-196 l/kg) (Aslam et al., 2015). The potential for Metolachlor-OA and
653 Metolachlor-EA retention in soils is relatively limited compared to S-Metolachlor. The
654 amount of S-Metalochlor stored in the soil profile at the end of the experiment (after 8
655 months) represents 65 % of the amount of S-Metolachlor measured in the soil profile at the
656 start of the experiment.

657 The second type of pesticides, actually a mixture of different compounds, was applied
658 during the tillering stage of wheat growth in April 2018. A total of 110 % of Mesosulfuron-
659 methyl, 48 % of mefenpyr-diethyl, 66 % of pinoxaden, and 82 % of cloquintocet-mexyl were

660 recovered in the petri dishes (Table 3). These values covered the total fraction of chemical
661 that reached the upper part of foliage and soil surface. We suppose that the low mass recovery
662 of the chemicals might be related to the low analytic recoveries of the water extraction
663 method used, and to pesticide volatilization during their application (Bedos et al., 2010). The
664 amount of chemicals that reached the soil surface the day of their application varied between
665 13 to 38 % of the amount initially applied by the farmer (Table 3). Chemicals were below
666 detection limits in the soil between 8 days following their applications and the end of
667 experiment. Pesticides export in drained water was not observed, mostly because of the low
668 concentration applied at the soil surface (between 15 and 50 g.ha⁻¹) and the interception of
669 herbicide by the plants.

670 The retention of these pesticides from spring application by the soil-plant continuum was
671 found equal to 100 %, which one might have thought significant, is related to the fact that the
672 herbicide was applied at a very low rate. We also have to keep in mind that if the parent
673 compound is well filtered by the soil, the same may not be true for their major transformation
674 products whose toxicity and behavior in the environment has recently emerged as an area of
675 concern (Reemstma et al., 2013).

676 **3.3 Interest and limits of our methodology**

677 A notable outcome of our research, insofar as the two functions related to the water budget are
678 concerned, is the observation that they cannot be inferred simply, as is routinely done for
679 example for the assessment of the water supply, through a classical water balance between
680 water lost by evapotranspiration and average precipitation. The hydrology of the site is
681 strongly influenced by the presence of artificial drains, which imperatively need to be taken
682 into account, especially for drains installed one or two centuries ago, their exact location is
683 unknown. Another result of the research is that a function, the provision of food by supplying

684 nutrients (in this case nitrogen) to crops, which one might have thought significant, turned out
685 to be marginally so, dwarfed as it is by the application of chemical fertilizers. In years to
686 come, as the industrial agriculture practiced at the site gets progressively replaced by more
687 sustainable forms of cropping, including organic farming (in high demand in the Paris region)
688 with high organic nitrogen inputs, it is likely that the importance of this function of the soil
689 will be strengthened once again, as records indicate it was until about 50 years ago.

690 The measurements carried out in our research constitute a very time-consuming effort,
691 which is not likely to be repeated frequently, and which, for the vast majority of undrained
692 soils, would present formidable challenges that are as yet unresolved. In table 2, we have
693 collected all the information related to the uncertainties associated with specific
694 measurements. Using a standard error propagation formula, we calculated an overall
695 uncertainty for each function from the errors determined from the available data. Table 2
696 show clearly show clearly that these estimated uncertainties are lower bounds, given the fact
697 that for several parameters, we have no uncertainty estimates. Also, in order to alleviate the
698 various assumptions that we have had to make in order to quantify soil functions, further
699 research will be necessary, involving additional measurements and, likely, increased costs.

700 **4. CONCLUSION**

701 The key outcome of the research described in this article is a detailed methodology to
702 measure directly a number of functions provided by soil. This methodology takes advantage
703 of a feature of the experimental site, an agricultural field in Saclay (France). The fact that this
704 field is artificially drained, and is underlain by a virtually impermeable clay layer at a
705 relatively shallow depth, allowed us to monitor the inputs and outputs of rain water, as well as
706 for nitrogen (added as fertilizer) and two types of herbicides, in the field site and to compute
707 accurate mass balances. Data resulting from this effort gave us the opportunity to quantify, for

708 the first time, three provisioning functions (supply of water to nearby stream, provision of
709 food by supplying, respectively, water and nitrogen to wheat crop), and three regulating
710 functions (flood mitigation, and filtration of, respectively, nutrients and herbicides).

711 Fortunately, now that actual, measured values of a selected number of functions are
712 available for the Saclay field, it becomes feasible for this site to evaluate to what extent
713 traditionally-used estimation methods, based on proxy data available in a recently developed
714 soil map of the Saclay plateau, or involving the mathematical modeling of soil functions, are
715 reliable. This follow-up research will be reported in future publications. It is clear however
716 that using proxies will very likely fail to precisely quantify functions that are strongly linked
717 to the soil functioning in time, as is the case with the water supply or the filtration of nutrients
718 and contaminants. A further challenge, not addressed here but nevertheless crucial, is to find a
719 way to quantify the other functions, including cultural ones, that have not been discussed in
720 the present article. One could argue that only when all of the relevant benefits derived by
721 humans from nature will be measured, will the “ecosystem services” framework represent a
722 workable option for decision-making (e.g., Baveye, 2017)

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916 **Table 1:** Main physical-chemical characteristics of the different horizons that are found in the soil at
 917 the experimental sit, above the impervious layer.

	LA (0-42cm)	BT (42-60cm)	BTg (60-85cm)	BTg/IC (85-100cm)	C/BTg (100-115cm)	Cca(g) (115- 135cm)	Cca (135- 180cm)
Clay, g kg ⁻¹	187	280	298	282	243	204	269
Silt, g kg ⁻¹	750	672	660	688	729	755	616
Sand, g kg ⁻¹	63	48	42	30	28	41	115
Bulk density, Mg.m ⁻³	<i>1.48*(±0.09)</i>	1.51 (±0.03)	1.54 (±0.03)	1.56 (±0.01)	1.59 (±0.02)	1.58 (±0.01)	
pH, H ₂ O	7.61	7.71	7.87	7.99	8.12	8.61	8.64
CEC, cmol(+) kg ⁻¹	11.2	14.6	16	16.2	15.1	12.8	17.8
OM, g kg ⁻¹	<i>16.4*(±0.5)</i>	7.7	5.0	4.6	2.8	2.8	2.5
SOC, g kg ⁻¹	<i>9.5*(±0.3)</i>	4.4	2.9	2.0	1.6	1.6	1.5
SN (total), g kg ⁻¹	<i>1.0*(±0.03)</i>	0.6	0.4	0.3	0.2	0.2	0.2
C/N	<i>9.8*(±0.01)</i>	7.7	7.4	7.2	7.1	7.9	7.4

918 * Italic style to represent measurements held in October 2017 (during the period of our study)

919 OM: organic matter

920 SOC: soil carbon content

921 SN: soil nitrogen content

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932 Table 2 : Site and soil attributes used to quantify the potential and actual state of the ecosystem to fulfill its function. We distinguish the category
 933 of attributes (grey color) about which we have direct information about the uncertainty associated with specific measurements used to calculate
 934 an overall uncertainty for the function
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Soil function (unit)	Value of the service rendered by the ecosystem % (unit)	Parameters/variables used for quantification of ecosystem services																
		Drain water (mm)	Soil water content at the beginning (mm)	Soil water content at the end (mm)	Rainfall (mm)	Water runoff (mm)	Soil hydraulic conductivity (mm/day)	Soil nitrogen content at the beginning (kg N ha ⁻¹)	Soil nitrogen content at the end (kg N ha ⁻¹)	N fertilizer	N uptake by plant (kg N ha ⁻¹)	N leached ((kg N ha ⁻¹)	N losses ((kg N ha ⁻¹)	Soil herbicide content at the beginning ((kg ha ⁻¹)	Soil herbicide content at the end ((kg ha ⁻¹)	Herbicide leached ((g ha ⁻¹)	Overall uncertainty of function % (standard error)	
Water supply to nearby stream % (mm)	53 % (334)	334 (±3) ^l																
Water supply to crop % (mm)	41 % (254)	334 (±3) ^l	154(±6)	82 (±4)	625	0											2% (±7)	
Nitrogen supply to crop % (kg N ha ⁻¹)	22 % (59.4)						61.7 (±15)	13.4 (±3)	251.3	268.9 (±45)	34.4	7.3					80% (±48)	
Flood mitigation % (mm/day)	100 % (746)						746 (±434)											58% (±434)
Filtering of nutrients % (kg N ha ⁻¹)	89.1 % (282)						61.7 (±15)	13.4 (±3)	251.3	268.9 (±45)	34.4	7.3						17% (±48)
Filtering of contaminants (g ha ⁻¹)	99.1 % (117)												118 (±62)	77 (±27)	1.1			58% (±68)

937 1 represent the error of manufacture of data

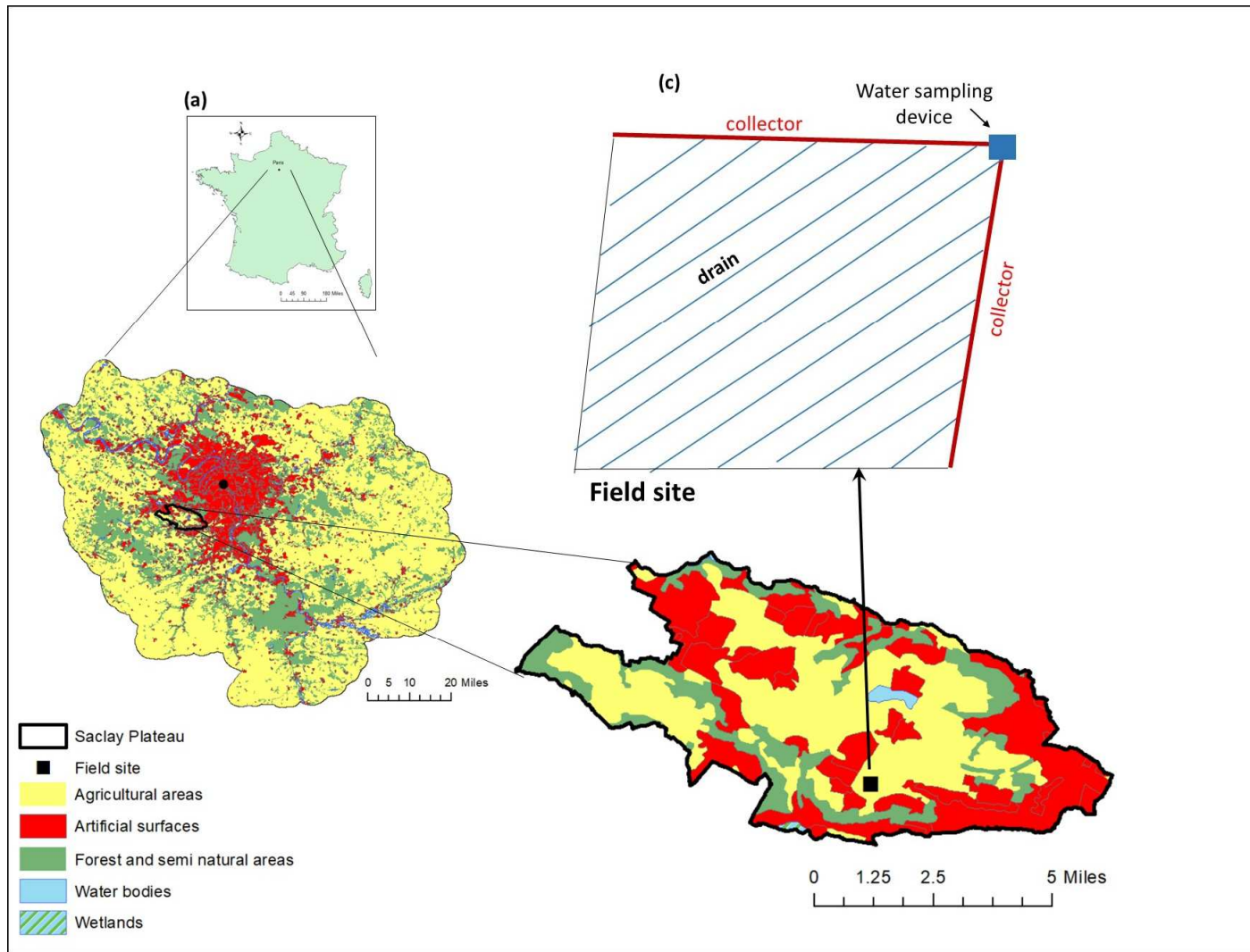
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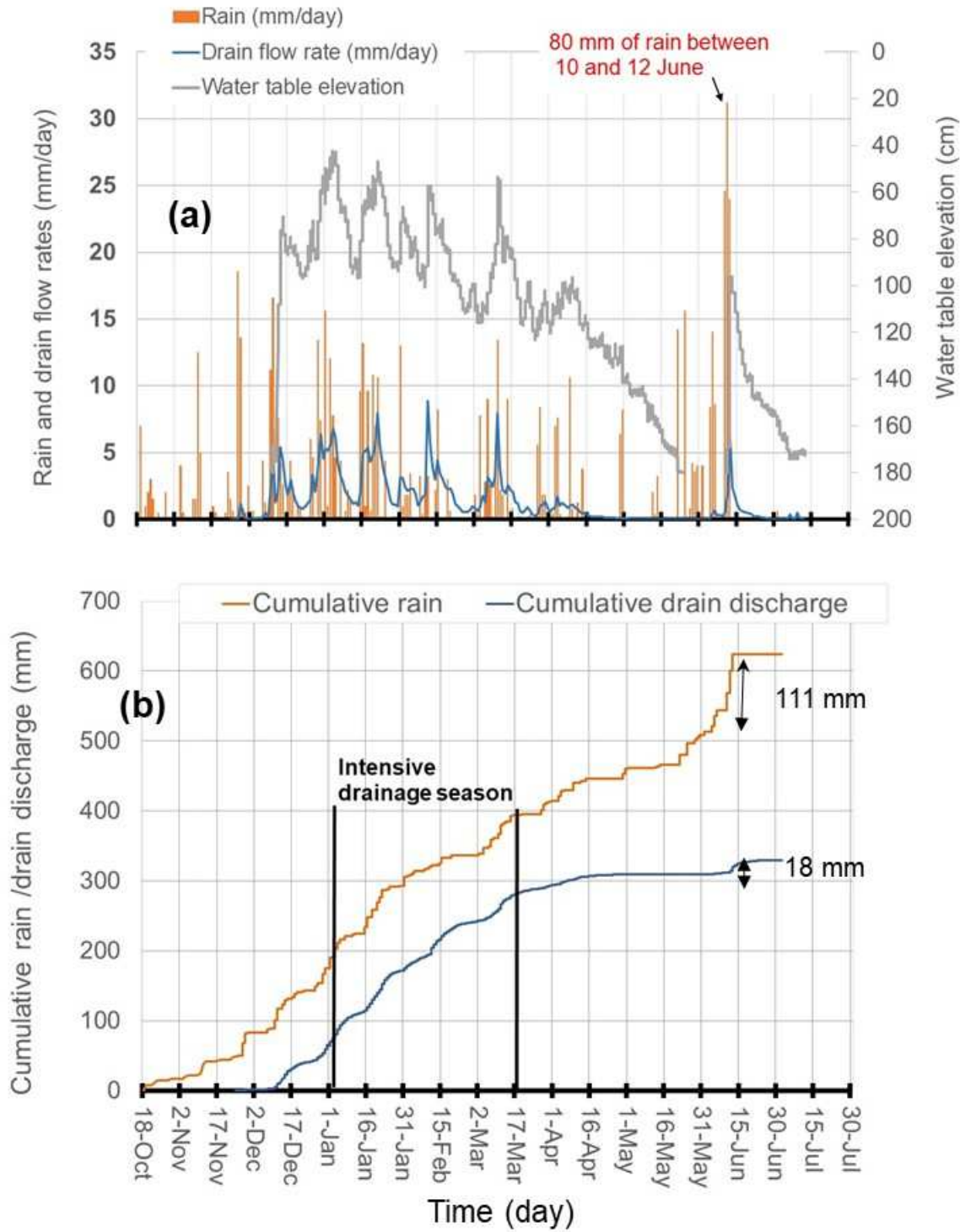
940 Table 3: Results of analyses of chemical applied in April 2018 in soil and drained water samples,
 941 amount expressed in brackets as percent of the amount applied at the soil surface by the farmer

		Mesosulfuron – Methyl (g ha ⁻¹)	Mefenpyr -diethyl (g ha ⁻¹)	Pinoxaden (g ha ⁻¹)	Cloquintocet -mexyl (g ha ⁻¹)
Soil	Day 0- Petri dishes	17±2.2 (111)	17±5.8 (38)	40±85.0 (66)	12±2.0 (82)
	Day 0- Soil below plant	6±0.0 (38)	8±2.0 (18)	13±3.8 (22)	2±0.0 (13)
	Day 97	NQ	NQ	NQ	NQ
Drained water	Day 6, 13,27...97	NQ	NQ	NQ	NQ

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947 **Figure 1.** (a) Location of experimental plot, (b) land use of the Ile de France” region according to
948 Corine digital land cover cartography (2015), (c) schematic of the layouts of the tile drainage systems
949 at the experimental sites

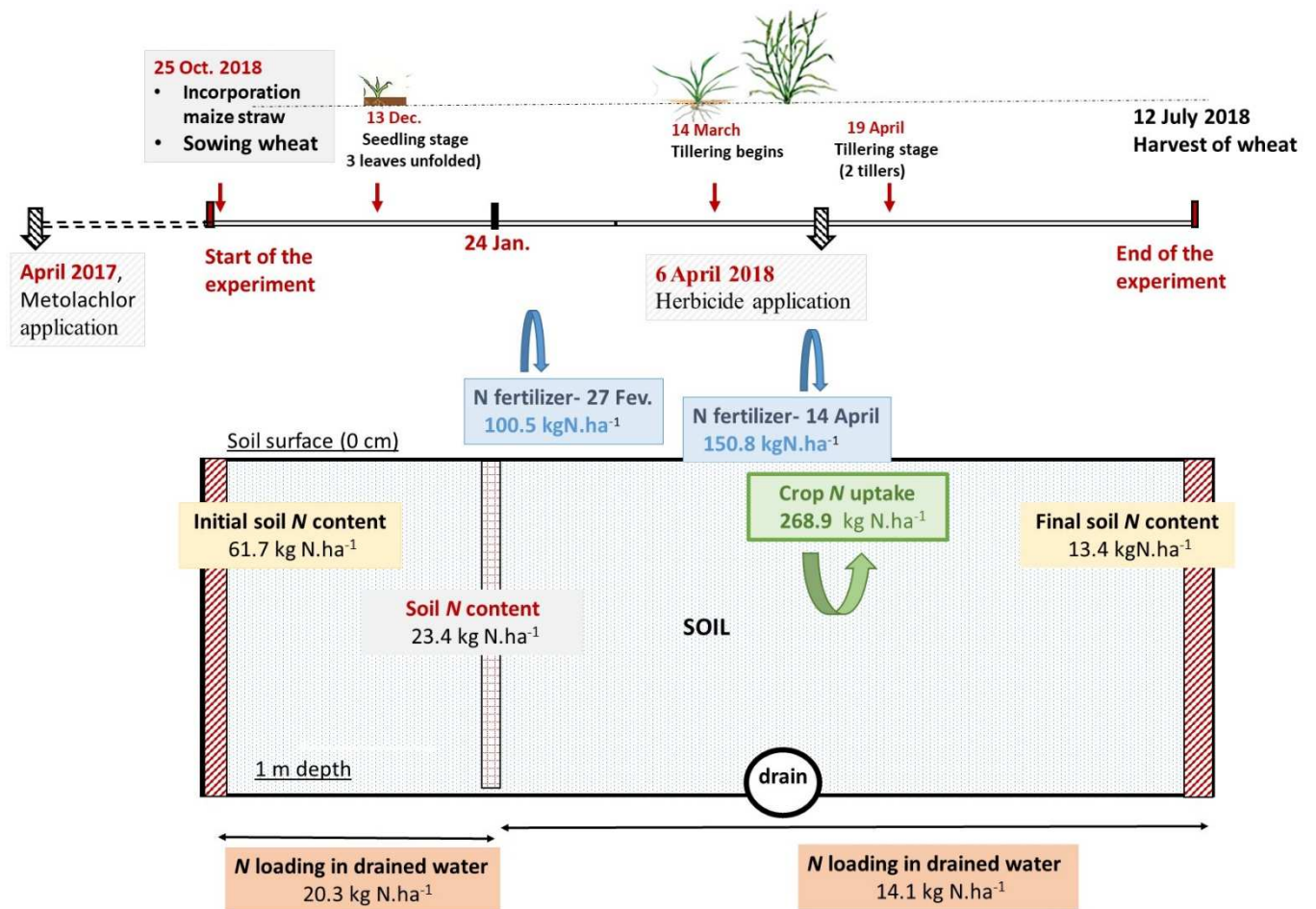


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955 **Figure 2.** (a) Fluctuations of soil water table elevations versus rainfall intensities and drain flow rates,

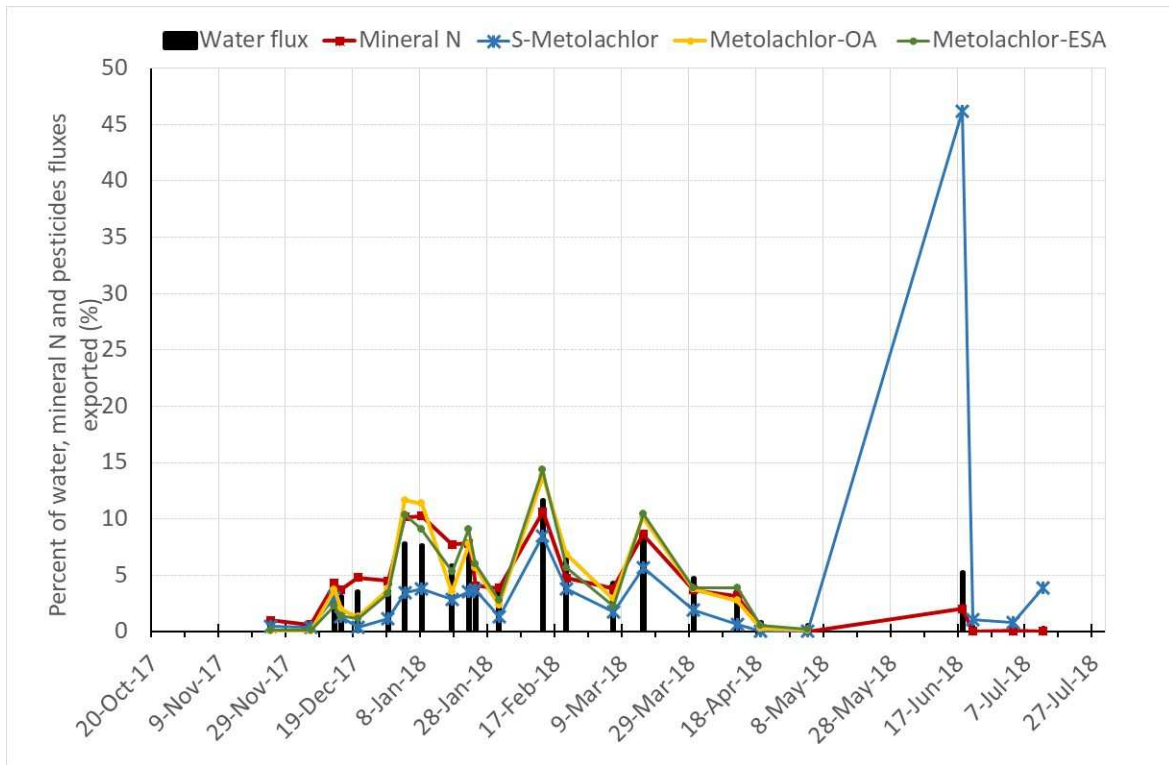
956 (b) temporal evolution of cumulative precipitation, drain discharge, and water table level.

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959 **Figure 3.** Nitrogen balance (kg N ha⁻¹) in the 0–100 cm soil layer, based on the measured values of N
 960 fluxes and accounting for mineral N fate at the field site.

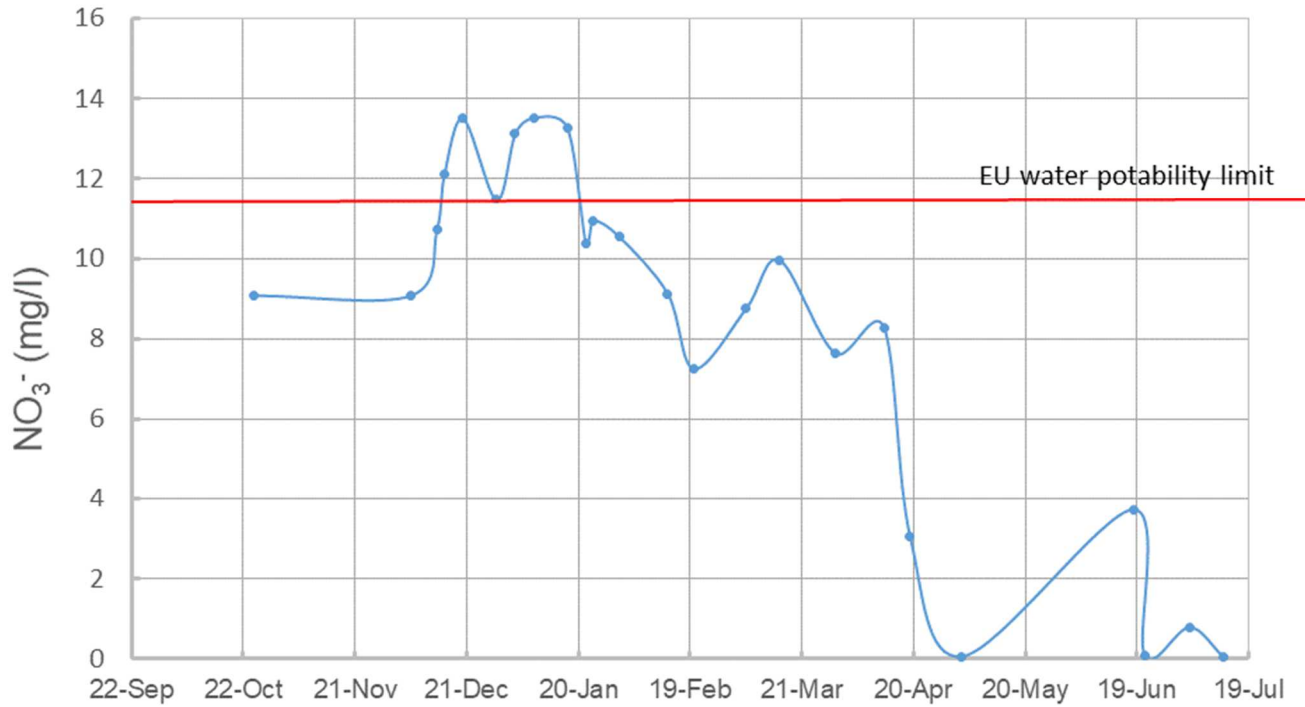


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962 **Figure 4.** Evolution of fluxes of water, mineral nitrogen and Metolachlor and its metabolites in the
 963 drain system as a percent of total water volume and amount observed over the whole drainage
 964 season

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974 **Figure 5.** Evolution of the nitrate concentrations in the drained water compared to threshold adopted

975 by the European Union

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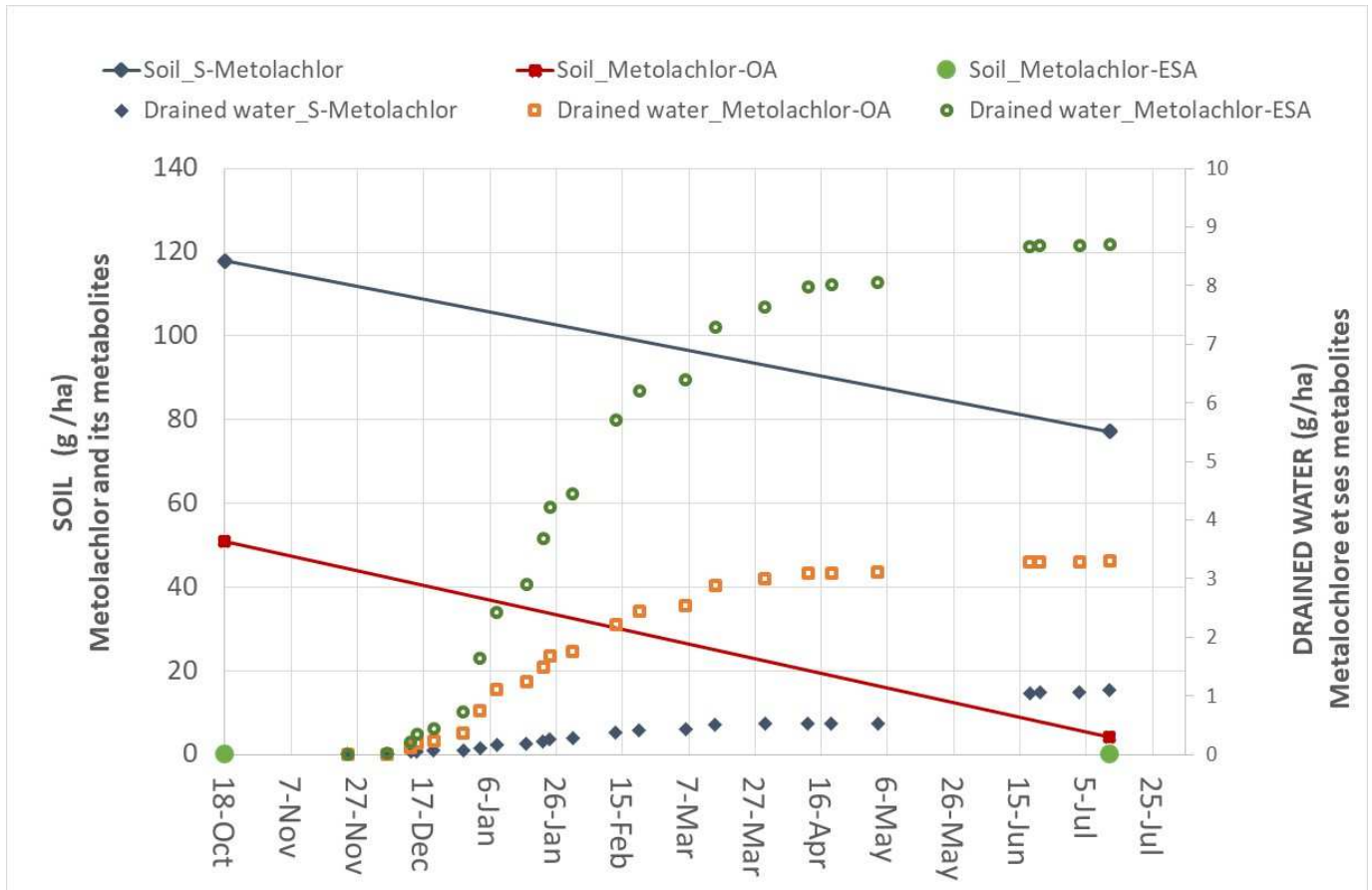
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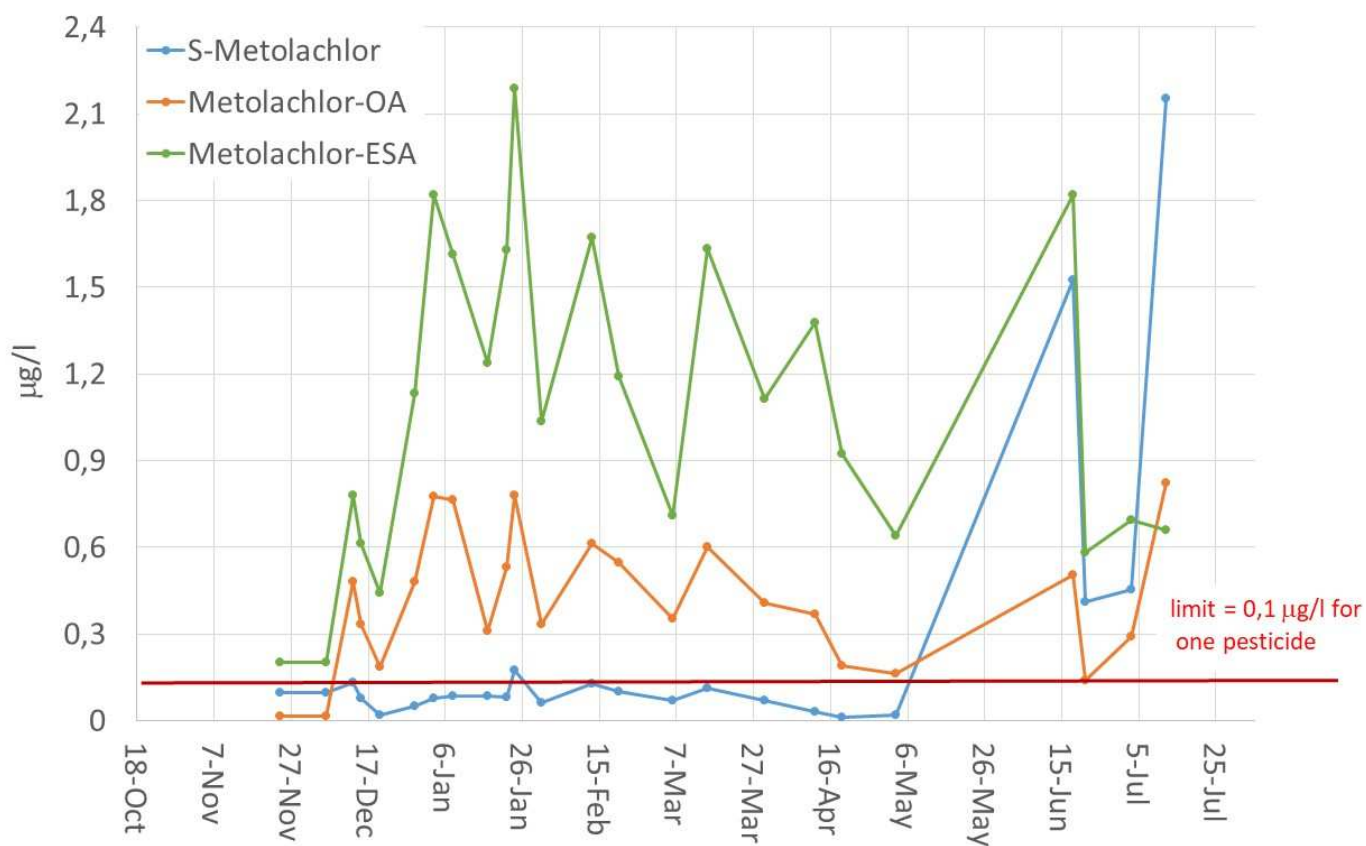
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984 Figure 6. Evolution over time of the amount of S-Metolachlor (cumulative: solid line) and its two

985 metabolites in the soil and drained water

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Figure 7. Evolution over time of the concentrations S-Metolachlor and its two metabolites in drained water compared to the threshold adopted by the European union (Farlin et al., 2018)