Direct measurement of selected soil services in a drained agricultural field: Methodology development and case study in Saclay (France)

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Abstract

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

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

1. Introduction

In the last few decades, the fact that soils fulfill an array of important functions, in particular for human societies, has become increasingly acknowledged by the public at large as well as by decision-makers. Aside from supplying water and nutrients to crops, a role that will become more and more crucial as the world's population rises to 10 billion people by the year 2050 (Foley et al., 2005), soils have a wide range of additional functions, e.g., providing support to various types of infrastructure (road, buildings), hosting a rich stock of genetic material, and serving to preserve archaeological artefacts (Blum, 1988 ; Baveye et al., 2016 ; Jónsson and Davíðsdóttir, 2016)[1]. Soils also store large amounts of organic matter, which if it were mineralized, would result in huge quantities of CO_2 being released into the atmosphere, potentially accelerating global warming. All these functions have been documented in detail by soil scientists over the last half-century (see, e.g., Baveye et al., 2016, for a comprehensive review). The topic now attracts yearly a steady stream of publications, and is the object of frequent conferences and symposia.

Because of widespread contamination, as well as sealing due to urban sprawl in many countries, soil resources are threatened worldwide, and it is urgent to manage them far more efficiently than was the case in the past. In order to do so, it is rapidly becoming imperative to be able to quantify explicitly the functions provided by soils, which would undoubtedly help to take into consideration the value of soil in the context of land management and urban planning. Various approaches have been explored in the past decade, and continue to be investigated to achieve this quantification. By using the data contained in soil survey maps 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).

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

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

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

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

2. Material and methods

2.1 Study area

The tile-drained agricultural field where the research was carried out is located on the Saclay plateau, in the "Ile de France" region, southwest of Paris (Figure 1). The field is located within a 80 km^2 peri-urban area currently undergoing urbanization in the context of the development of the "Paris-Saclay Université" project, touted as France's top research, innovation and business cluster. The geological stratification of the plateau is typical of the Parisian Basin. A layer of loam with a variable thickness covers a burrstone clay bed, called "Argile à Meulières," which lays atop the sand and sandstone of the "Sables de Fontainebleau" formation (Nicole et al., 2003).

Measurements at the site took place over the crop cycle extending between the 20th of October 2017 and the 12th of July 2018, on a 1.71 hectare plot subjected to agricultural practices that are routinely practiced in the region. The soil was tilled on the 25th of October to a depth of 30 cm with incorporation of residues of the previous year's crop (i.e., maize straw). Winter wheat (Lg Absalon) was planted the same day and was harvested on the 12th of July. N fertilizer was applied as NH_4NO_3 on the 27th of February at a dose of 100.5 kg N ha^{-1} and on 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} over the growing season. When wheat reached the tillering stage, on the 6th of April 2018, the field received an application of mesosulfuron-methyl, mefenpyr-diethyl, pinoxaden and cloquintocet-mexyl, equivalent respectively to doses of 0.015, 0.045, 0.06, and 0.015 kg ha^{-1}. During the previous maize growing season, on April 27, 2017, S-Metolachlor had been sprayed on the field, at a dose of 1.92 kg ha^{-1}.

The experimental plot is equipped with an independent and individual drainage system allowing to isolate with good confidence the contribution of the study area from adjacent fields having different land uses. The site has subsurface drains (perforated polyethylene pipe internal diameter = 4.4 cm;) at a depth of 1 m, and with a lateral 12 m spacing between adjacent drains. The outlets of the drains are connected to a collector drain with a larger inner diameter (d= 15 cm), discharging into an open drainage ditch (Figure 1).

A 2.5 m-deep trench was dug in May 2017 to describe and sample the different horizons in the soil profile. The soil is classified as a silt loam Glossic Luvisol (IUSS Working Group WRB, 2015). Its main physico-chemical characteristics are reported in Table 1. Characteristics supposed to change with time in the upper horizon, like soil organic matter and nitrogen, were re-analyzed at the beginning of the monitoring period (October 2017). Average bulk density profiles were measured in each horizon in triplicate using 500-cm^3 soil cores (9 cm by 8.4-cm diameter). Field observations reveal the presence of a burrstone clay layer at a depth between 1.8 and 2 m. Although water may still infiltrate through this type of formation (Nicole et al. 2003), these fluxes are of little spatial extent and made less active owing the drainage system. An evidence of this is the fact that the observation of a perched water table, and the fact that the soil became rapidly waterlogged when the drainage outlet was accidently cut. Thus, water flow below the clay formation is likely to make up a small fraction of the total water balance (a few mm to a maximum of 20 mm / year) and that when the soil above the clay layer becomes waterlogged, the only way for the water to leave is through the subsurface drainage network during winter time, and through evapotranspiration during other seasons.

2.2 Field assessment of ES in the field

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

2.2.1 Provisioning Services

Water supply to nearby stream

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

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

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

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

m^3 of liquid flowed past the flow meter, the logger registered one pulse input. When a predetermined number of pulses was reached, the logger sent a signal to the sampler to collect one individual 100 ml sample. These individual samples, collected at equal increments of flow volume, were combined into a single container (25 l) to form a composite sample, representing an average of the characteristics (e.g., nitrogen content) of the drain flow over the time increment considered.

Provision of food by supplying water to crops

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

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

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

where *ET* denotes evapotranspiration, SW (mm) is the product of the volumetric moisture content θ_v and a depth h (mm) of the soil profile, and represents the amount of water (expressed as an equivalent water height) present in the soil profile down to a depth h (mm), $(SW_i - SW_f)$ is the variation of the soil water content in the soil profile between the start and the end of the monitoring period, $\sum_{i=1}^{t} P$ and $\sum_{i=1}^{t} R$ are, respectively, the amount of rainfall and water runoff at the soil surface during the same time. Since visual observation during the entire growing season does not provide evidence of surface runoff, the latter is assumed negligible in eq. (2). Q is the amount of drained water calculated from eq. (1).

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

In our experiments, the volumetric moisture content θ_v was measured by taking soil samples respectively on the 20th of October 2017 and the 12th of July 2018. At each sampling date, three composite samples were taken in the field (10 m apart). Each composite sample was made up of three discrete subsamples obtained in a 1x 1 m area and homogenized to ensure that portions of the composite samples subsequently used for analysis were representative of the whole samples. In total, nine soil cores were sampled down to 1m and pooled into three composite samples for each depth. The cores were cut in 30 cm increments down to 60 cm and in 40 cm increment from 60 cm to 1 m. Each composite sample, after homogenization, was split into three parts for water, nitrogen and pesticide analysis. Soil bulk density of the plough layer was measured in triplicate using 100-cm^3 soil cores (2.5 cm by 5-cm diameter). Each sample had its gravimetric water content measured and converted to volumetric water content using the average bulk density profiles (Table 1). The amount of rainfall, P**,** was recorded on site at a time step of 15 min. Additional daily weather data (air temperature, air humidity, wind speed, and net radiation) were recorded at a meteorological station located 500 m away from the field experiment.

Provision of food by supplying nitrogen to crops

Soils provide various nutrients to crops and, in principle, this function could be analyzed separately for each nutrient, be it major or minor. In our experiment, we focused on nitrogen, an essential nutrient. At the beginning of the crop growing season, a portion of the nitrogen present in the soil is in mineral form, and another is associated with organic matter. During the growing season, nitrogen is added to the soil through application of fertilizers, and some nitrogen gets lost through drainage, or by denitrification or NH_3 volatilization at the soil surface. During the span of a single growing season, one can consider that the soil nitrogen taken by plants, N_{uptake}, does not come only from fertilizers but also from (i) the mineralization of soil organic matter by microorganisms N_{SOM}, which makes nitrogen available to crops, and (ii) from the initial stock, $N_{initial}$, of nitrogen in the soil (Therond et al., 2017).

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

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

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

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

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

Each of the terms in this mass balance was estimated as follows. The difference ($\boldsymbol{N_{initial}}$ **-** $\boldsymbol{N_{final}}$) in the soil down to the drains (at 1 m depth) was established on the basis of soil samples obtained on 20 October 2017 and 12 July 2018, as described before. Mineral N was extracted on fresh homogenized soil samples during one hour (50 g soil/100 mL 1 M KCl) and analyzed by colorimetry using a continuous flow analyzer (Skalar, Breda, The Netherlands) for N-NH_4^+ and N-NO_3^-. The analytical results expressed as concentrations were converted to kg per ha using measured soil bulk density values (Table 1). Information on fertilizer use by the person farming on the experimental site provided the value of $\boldsymbol{N_{fertilizer}}$. The following term, $\boldsymbol{N_{uptake}}$, was measured by sampling the aboveground plant biomass (aerial biomass and grain yields) in three 2-m^2 plots located 10 m away from each other. Nitrogen stored within roots was considered to be equivalent to 25 % of the measured aboveground plant biomass N content. The total dry matters (t ha^{-1}) of the aerial biomass and the grain yields were calculated based on the moisture content of the aerial and grain subsamples. The total N contents in the grains and aerial biomass (stems plus leaves) were determined by elemental analysis. $\boldsymbol{N_{leach}}$, the amount of inorganic N leached during the experiment, was measured in the subsamples of the drainage water collected with the water sampling system described before. Mineral nitrogen was analysed by colorimetry using a continuous flow analyser (Skalar, Breda, The Netherlands) for N-NH_4^+ and N-NO_3^-. Finally, N_{losses}, nitrogen losses by volatilization and denitrification following fertilizer application, was estimated to be equal to 7.3 kg N ha^{-1} according to literature for comparable conditions (crop type, climatic conditions, fertilizer): nitrogen losses by volatilization (N-NH_3) was fixed to 1 kg N ha^{-1} according to Ramanantenasoa et al. (2018); N-N_2O emission by denitrification was fixed to

2.5 % of the applied N according to the work of Henault et al. (1998), who measured N-NO_2 fluxes during 5 months following NH_4-NO_3 fertilizer application for an experimental plot located on a similar soil type (hydromorphic gleyic Luvisol) and also cropped with wheat.

2.2.2 Regulating services

Flood mitigation

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

Filtration of nutrients (Nitrogen)

The traditional perspective on this function (e.g., Blum, 1988; Dominati et al., 2014; Baveye et al., 2016) is that it corresponds to the retention by the soil of nitrogen applied at the surface or produced internally. The key outcome of this process, when the function is fulfilled, is that a tolerable amount of nitrogen reaches groundwater resources, or as is the case on the Saclay plateau, is directly discharged into nearby streams. To quantify this function, one approach is to relate the amount of nitrogen that is leached to the amount that is either applied or internally produced (Villamagna et al;, 2013; Therond et al., 2017). It is defined here as the nitrogen retained in the soil, expressed as a proportion of total mineral N considered as inputs in the soil system. From that perspective, the effectiveness of the soil in supplying this service can be quantified as follow

$$N_{filtered}\,(\%) = \left(1 - \frac{N_{leach}}{N_{initial} + N_{fertiliser} - N_{losses} + N_{SOM}}\right).100 \qquad (5)$$

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

Filtration of contaminants (Herbicides)

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

$$herbicide_{filtered}\,(\%) = \left(1 - \frac{herbicide_{leach}}{herbicide_{initial} + herbicide_{added}}\right).100 \qquad (6)$$

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

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

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

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

SPE) clean-up were optimized following Anastassiades et al. (2003). The procedure involves initial single-phase extraction of 10 g sample with acetonitrile, followed by liquid–liquid partitioning by addition of anhydrous $MgSO_4$ and NaCl. Removal of residual water and cleanup are performed simultaneously by using a procedure called dispersive solid-phase extraction (dispersive-SPE), in which anhydrous $MgSO_4$ and primary secondary amine sorbent are mixed with acetonitrile extract. An aliquot of the final extract is taken for analysis by LC/MS.MS. In parallel, a multi-residues analysis by GC-ECD/FPD is performed on the ethyl acetate extract solvent. Quantification of the pesticide residues was carried out by liquid chromatography-tandem mass spectrometry (LC-MS.MS), gas chromatography–electron-capture detection (GC-ECD). The recovery rates ranged from 79% to 106%. The limit of quantification was 10 µg/kg for soil extracts and 0.05 µg/L for drained water samples.

2.2. 3 Uncertainty analysis

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

$$var\ q = var\ x + \cdots var\ \mathrm{w} \qquad (7)$$

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

3. RESULTS AND DISCUSSION

3.1 Provisioning Services

Water supply to nearby streams

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

To better understand the temporal furniture of the service of water supply, the drainage period was split in three key periods (Figure 2 b). During the first period, from October 18, 2017, to the end of December, the cumulative rainfall curve rises steadily, unlike the cumulative drainage one, which takes off only after December 10, and even then at a slower rate. The cumulative drainage between November 28 and December 31 corresponds to about 32% of the cumulative rainfall, which implies that about 68% of the rainfall does not contribute to water supply during that period. A second period, which can be characterized as a time of intensive drainage, extends approximately from the end of December until the 13th of March 2018. During that period, the cumulative drainage curve runs roughly parallel to the cumulative rainfall one, which means that 100% of the rain (equivalent to a 209 mm layer) contributed to water supply. The third period of drainage (from the 13st of April onward) is characterized by less frequent rainfall events, and an increase of the evaporative demand, which results in a flat cumulative drainage curve for much of the time, and a continuous drop of the water table, below two meters even in late early June. During this last period, only 24 % of the rainfall contributed to water supply. As a result, more rainfall during the time of intensive drainage systematically induces an increasing water supply while it is far less the case outside of the intensive drainage period.

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

Provision of food by supplying water to wheat crop

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

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

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

The (potential) supply of water to crop is estimated through a great diversity of indicators among which the water retention potential (Grimaldi et al., 2014; Calzolari et al., 2016). The water retention potential of the first 100 cm of the studied soil was estimated to range from 153 to 200 mm depending on the pedotransfer function used (Predal A., 2018). The classical estimation of the water retention potential from granulometric information available in soil maps thus underestimated the real supply of water to crops by 54 to 101 mm, which is not surprising as the water retention potential is regularly refilled during the crop growth. If the underestimation appears limited in the considered case and the water retention potential as a suitable proxy to assess the water supply function/service, this is very likely because i) the soil under study received an adequate amount of rainfall (625 mm) compared to the potential and actual need of the crop and atmosphere (*ETc* = 423 and *ET* = 363 mm), ii) the entire soil profile is very well and uniformly colonized by roots, iii) the high soil hydraulic conductivity at saturation (with an average of 746 mm/day) is indicative of “ideal” conditions for the redistribution of crop-available water (Topp et al., 1997; Reynolds et al., 2003); and finally iv) the land drainage evacuated the water in excess out of the root zone. Such ‘ideal’ conditions are however not the rule and the water retention potential may consequently be less efficient than measured here to assess the real water supply to crops.

Provision of food by supplying nitrogen to crops

Mass balance calculations, as described schematically in Figure 3, allow us to determine the amount of nitrogen that is directly supplied to crops by the mineralization of soil nitrogen. 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 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 with a literature-based estimate of N_{losses} (7.3 kg N ha^{-1}), it is possible through eq. (4) to calculate N_{som}, whose value is equal to 11.1 kg N ha^{-1}.

The outcome of these calculations is that the total sum of the N that is directly or indirectly contributed by the soil itself and potentially used by crop, i.e., the sum of the change in soil mineral nitrogen content between the beginning (mainly released by mineralization of soil organic matter in last summer) and the end of the experiment, and the nitrogen produced by mineralization of organic matter during the experiment, was found equal to 59.4 kgN.ha^{-1}. This represents 22 % of the measured crop N uptake, in line with other studies (e.g., Palmer et al., 2017), which found that in agroecosystems where N was not limiting growth (i.e., when fertilizer applications were sufficiently high), the nitrogen supplied to crops by fertilizer application dominated the amount of N derived from mineralization of soil organic matter. The standard error propagation formula calculate an overall uncertainty for this ES equal to 80 %, which is quite significant. Plant N uptake was the major source of this high uncertainty (Table 2).

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

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

3.2 Regulating services

Flood mitigation

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

To prevent ponding at the surface, the drainage system has to be able to evacuate water fast enough so that the water table never reaches that level. Measurements of the water table elevations over time (Figure 2 a) show that the water table level did not come up above 40 cm below the surface, even after rainfall events of high intensities. Therefore, the drainage system is working as expected, but in terms of the broader hydrological scene in the area, drainage of a field cannot be too rapid. Given the size of the Saclay plateau, if in each field, drains start releasing water to nearby ditches within minutes after a rainfall event, there would be a sizeable risk of flooding downstream.

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

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

Filtering of nutrients (Nitrogen)

The filtering of nutrients at the field site, was computed according to equation (5), which takes into account the initial stock of mineral N (61.7 kg N ha^{-1}), N losses that may occur in the system (34.4 kg N ha^{-1}), as well as the amount of nitrogen mineralized from the soil organic matter (11.1 kg N ha^{-1}). This calculation yields a value of $N_{filtered}$ = 89.1 %, implying that 10.9% of the nitrogen that is applied to the soil or is produced internally ends up in the drain. This is still a somewhat high number, and one could consider that the ability of the soil to filter nitrogen is not optimal. The overall uncertainty for this function by computing errors of parameters for which we have values (Table 2) was 17 % under the conditions of this study.

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

Again, as with the previous function, the filtering of nutrients at the field site can be interpreted in different ways according to the beneficiary of the function. Another perspective, which is likely to be adopted by farmers concerned about the (financial) bottom line, consists of considering only the amount of nitrogen that is applied as fertilizer at the soil surface during the growing season, and the amount that leaves the field site in the drain water. According to this "black box" approach, 251.3 kg N ha^{-1} are applied, and 34.4 kg N ha^{-1} leave the site, which can be interpreted to mean that a relatively sizeable 13.7 % of the fertilizer applied to the field is not filtered by the soil and ends up in the nearby ditch. From an economic viewpoint, these 13.7 % are a net loss, which the farmer could conceivably try to reduce, for example by adapting application rate according to crop demand using precision farming.

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

Filtering of contaminants (Herbicides)

The first type of pesticide, S-Metolachlor, was applied at a rate of 1920 g ha^{-1} on 27 April 2017 before the beginning of our experiment. Analysis of S-Metolachlor within the soil profile on October 20, 2017, showed a soil concentration of 26 µg/kg and 2 µg/kg in the 0-30 cm, 30-60 cm soil layers. S-Metolachlor concentrations were below detection limits in the soil layer from 60 to 90 cm. These concentrations, converted to g per ha using the bulk density values, are equivalent to 118 g.ha^{-1} in the whole profile (Figure 6). S-Metolachlor concentration in soil decreased to 77 g. ha^{-1} within the whole soil profile at the end of experiment. The cumulative amount of S-Metolachlor exported in drained water has been recorded equal to 1.1 g.ha^{-1} during the period of our experiment. From equation (6), the retention of S-Metolachlor by the soil was found equal to 99.1 % by relating the amount of herbicide that is leached during the monitoring period ($herbicide_{leach}$ = 1.1 g.ha^{-1}) to the amount observed within the soil profile on October 25, 2017 ($herbicide_{initial}$ =118 g.ha^{-1}). The standard error propagation formula calculate an overall uncertainty for this ES equal to 58 %, which is quite significant. S-Metolachlor concentrations in soil was the major source of this uncertainty (Table 2). The retention of S-Metolachlor could not be evaluated from the date of its application (April) because the amount of S-Metolachlor that is leached between April and October is unknown.

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

The parent compound, S-Metolachlor, exhibited a particular behavior during the period following the high rainfall events at the beginning of June. S-Metolachlor concentrations in the drained water increased 19 and 27 times, respectively, on June 18 and July 12, compared to the average for the rest of time. The higher amount of this chemical lost during this period could be related to the extremely high amount of rain (111m equivalent) that occurred during a very short time span.

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

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

The second type of pesticides, actually a mixture of different compounds, was applied during the tillering stage of wheat growth in April 2018. A total of 110 % of Mesosulfuron-methyl, 48 % of mefenpyr-diethyl, 66 % of pinoxaden, and 82 % of cloquintocet-mexyl were recovered in the petri dishes (Table 3). These values covered the total fraction of chemical that reached the upper part of foliage and soil surface. We suppose that the low mass recovery of the chemicals might be related to the low analytic recoveries of the water extraction method used, and to pesticide volatilization during their application (Bedos et al., 2010). The amount of chemicals that reached the soil surface the day of their application varied between 13 to 38 % of the amount initially applied by the farmer (Table 3). Chemicals were below detection limits in the soil between 8 days following their applications and the end of experiment. Pesticides export in drained water was not observed, mostly because of the low concentration applied at the soil surface (between 15 and 50 $g.ha^{-1}$) and the interception of herbicide by the plants.

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

3.3 Interest and limits of our methodology

A notable outcome of our research, insofar as the two functions related to the water budget are concerned, is the observation that they cannot be inferred simply, as is routinely done for example for the assessment of the water supply, through a classical water balance between water lost by evapotranspiration and average precipitation. The hydrology of the site is strongly influenced by the presence of artificial drains, which imperatively need to be taken into account, especially for drains installed one or two centuries ago, their exact location is unknown. Another result of the research is that a function, the provision of food by supplying nutrients (in this case nitrogen) to crops, which one might have thought significant, turned out to be marginally so, dwarfed as it is by the application of chemical fertilizers. In years to come, as the industrial agriculture practiced at the site gets progressively replaced by more sustainable forms of cropping, including organic farming (in high demand in the Paris region) with high organic nitrogen inputs, it is likely that the importance of this function of the soil will be strengthened once again, as records indicate it was until about 50 years ago.

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

4. CONCLUSION

The key outcome of the research described in this article is a detailed methodology to measure directly a number of functions provided by soil. This methodology takes advantage of a feature of the experimental site, an agricultural field in Saclay (France). The fact that this field is artificially drained, and is underlain by a virtually impermeable clay layer at a relatively shallow depth, allowed us to monitor the inputs and outputs of rain water, as well as for nitrogen (added as fertilizer) and two types of herbicides, in the field site and to compute accurate mass balances. Data resulting from this effort gave us the opportunity to quantify, for the first time, three provisioning functions (supply of water to nearby stream, provision of food by supplying, respectively, water and nitrogen to wheat crop), and three regulating functions (flood mitigation, and filtration of, respectively, nutrients and herbicides).

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

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Table 1: Main physical-chemical characteristics of the different horizons that are found in the soil at 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}	*1.48[*] (±0.09)*	1.51 (±0.03)	1.54 (±0.03)	1.56 (±0.01)	1.59 (±0.02)	1.58 (±0.01)	
pH, H_2O	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}	*16.4[*](±0.5)*	7.7	5.0	4.6	2.8	2.8	2.5
SOC, g kg^{-1}	9.5[*]*(±0.3)*	4.4	2.9	2.0	1.6	1.6	1.5
SN (total), g kg^{-1}	*1.0[*](±0.03)*	0.6	0.4	0.3	0.2	0.2	0.2
C/N	*9.8[*](±0.01)*	7.7	7.4	7.2	7.1	7.9	7.4

[*] Italic style to represent measurements held in October 2017 (during the period of our study)
OM: organic matter
SOC: soil carbon content
SN: soil nitrogen content

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 of attributes (grey color) about which we have direct information about the uncertainty associated with specific measurements used to calculate an overall uncertainty for the function

		Parameters/variables used for quantification of ecosystem services															
Soil function (unit)	Value of the service rendered by the ecosystem % (unit)	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)*[1]															
Water supply to crop % (mm)	41 % (254)	334 *(±3)*[1]	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)

[1] represent the error of manufacture data

Table 3: Results of analyses of chemical applied in April 2018 in soil and drained water samples, 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

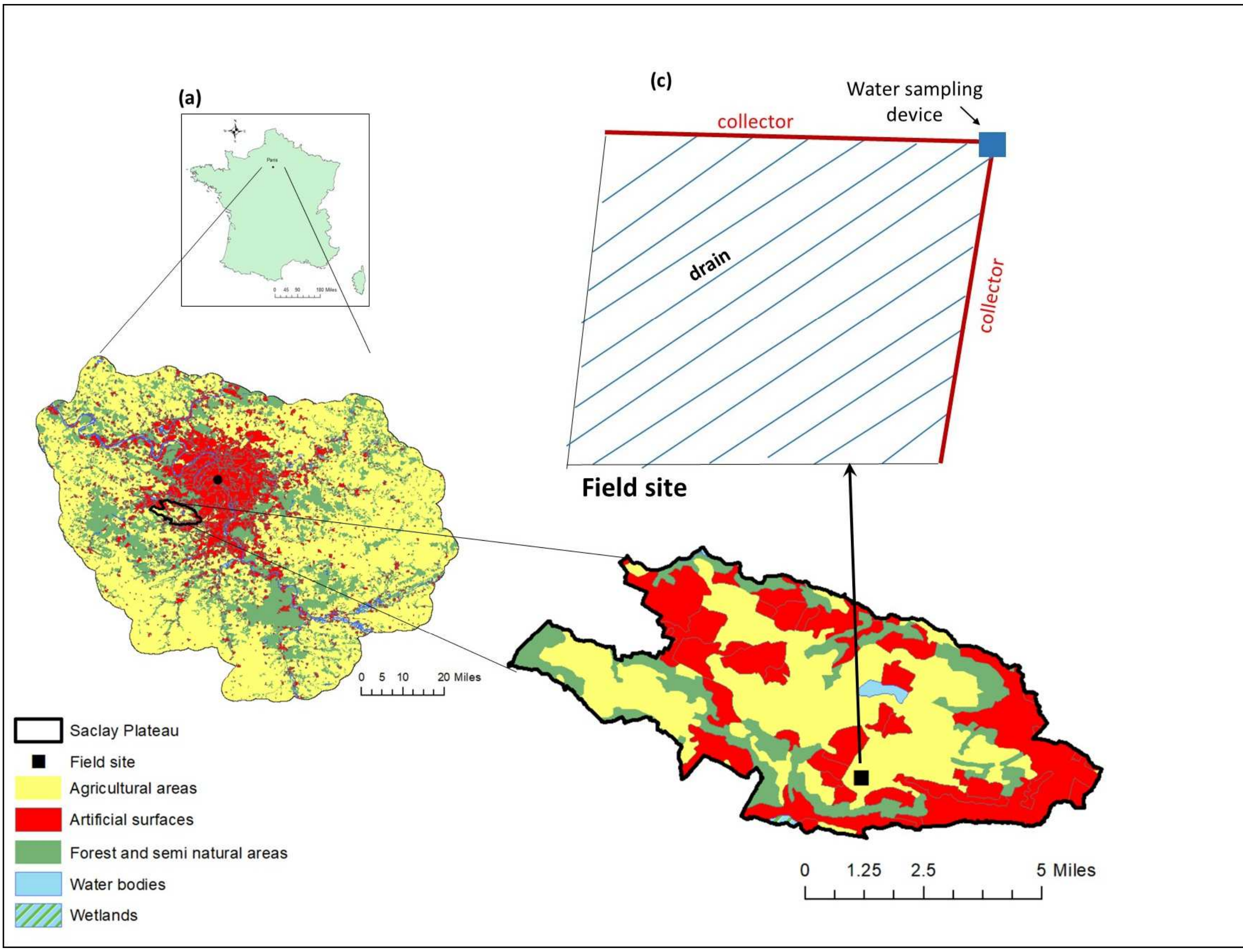
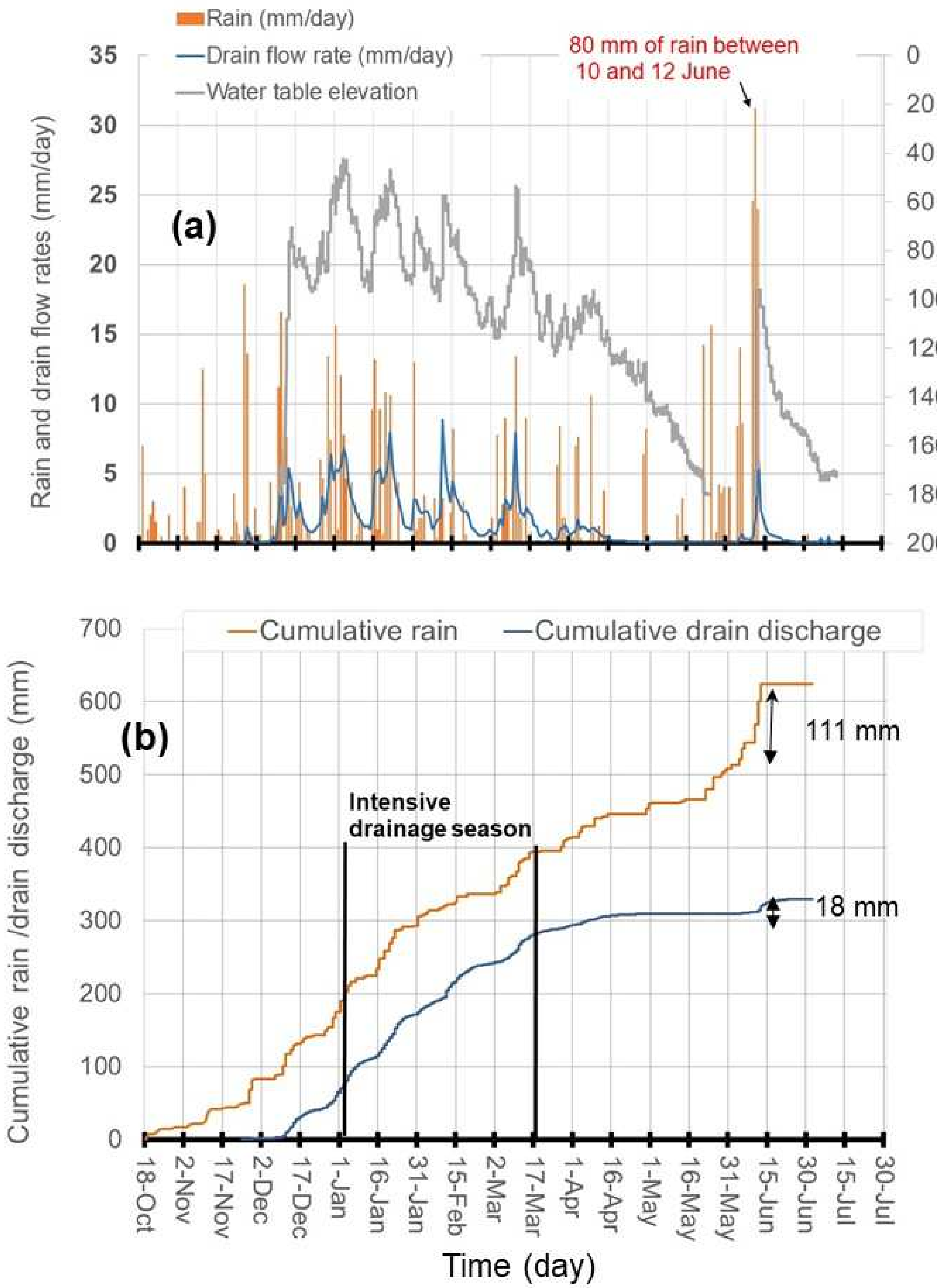


Figure 1. (a) Location of experimental plot, (b) land use of the Ile de France" region according to Corine digital land cover cartography (2015), (c) schematic of the layouts of the tile drainage systems at the experimental sites



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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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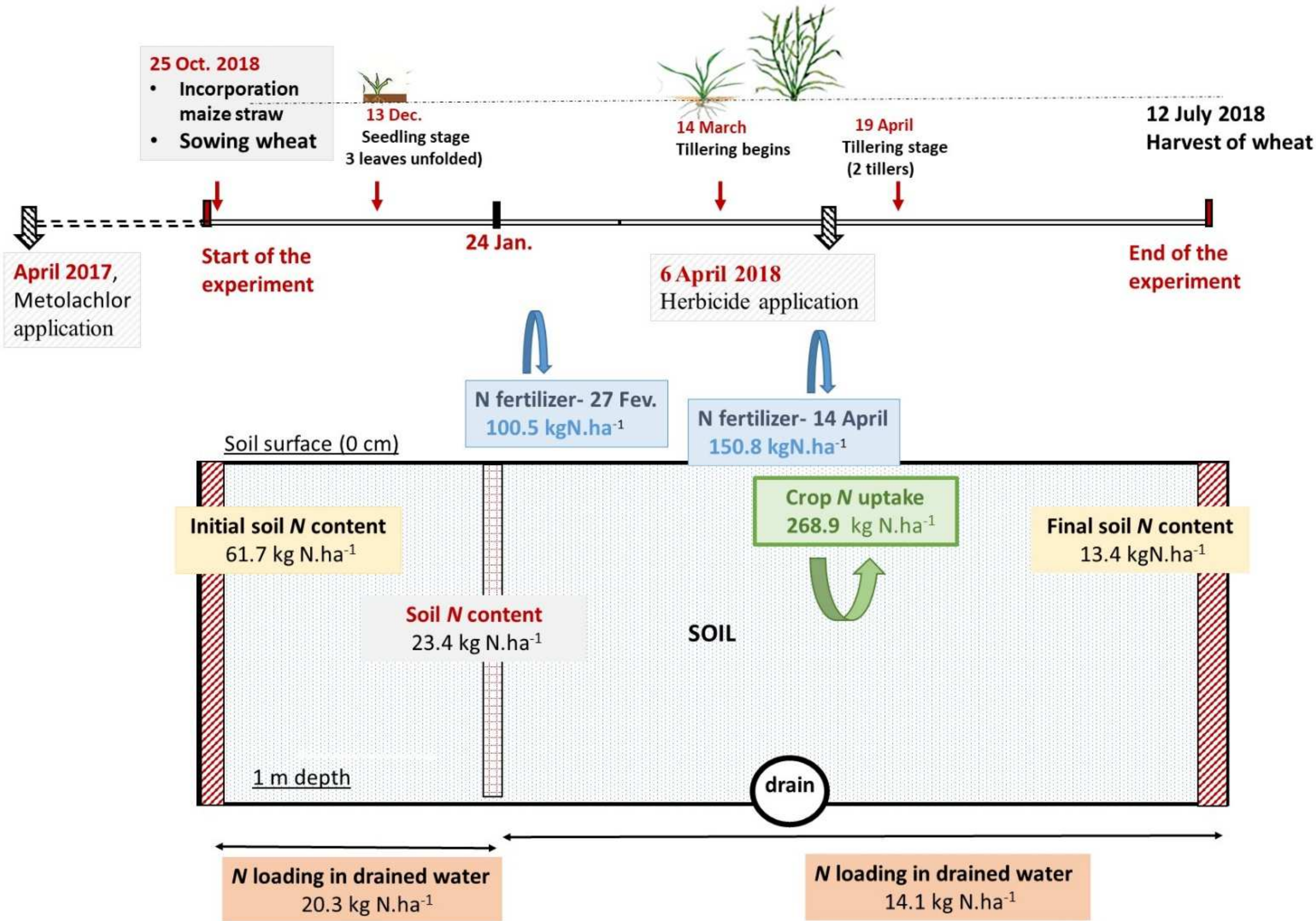
958 

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.

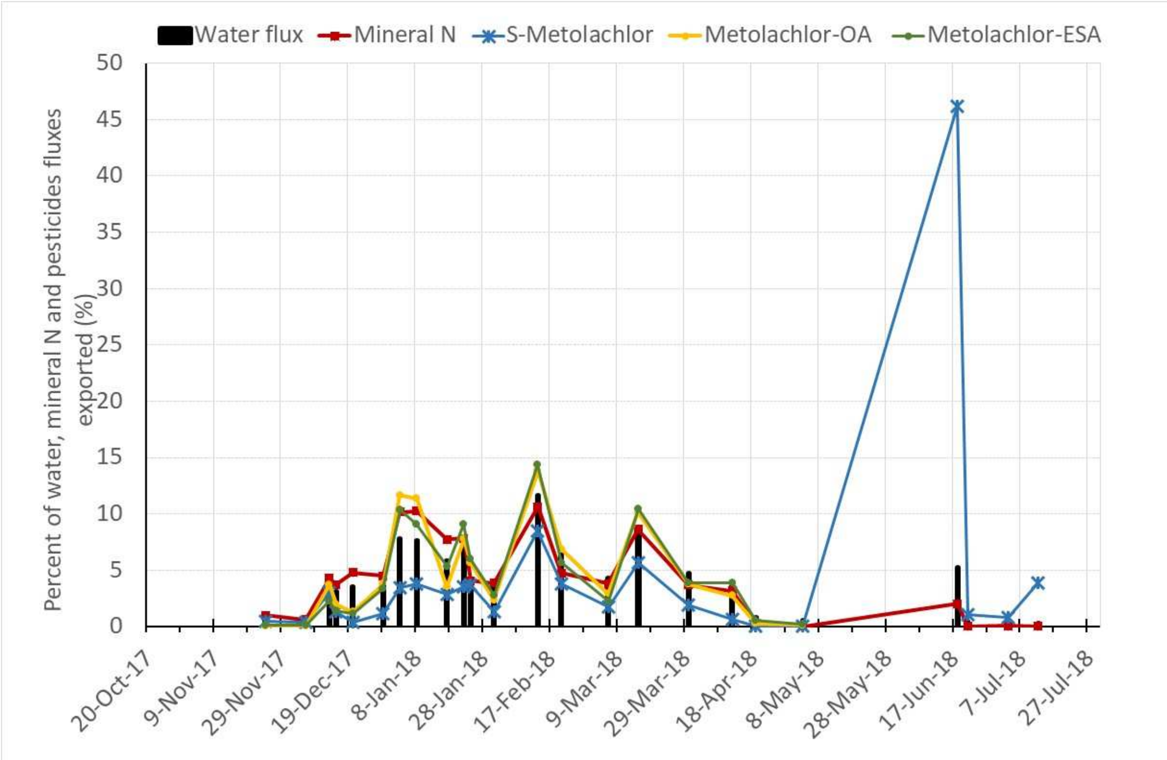


Figure 4. Evolution of fluxes of water, mineral nitrogen and Metolachlor and its metabolites in the drain system as a percent of total water volume and amount observed over the whole drainage season

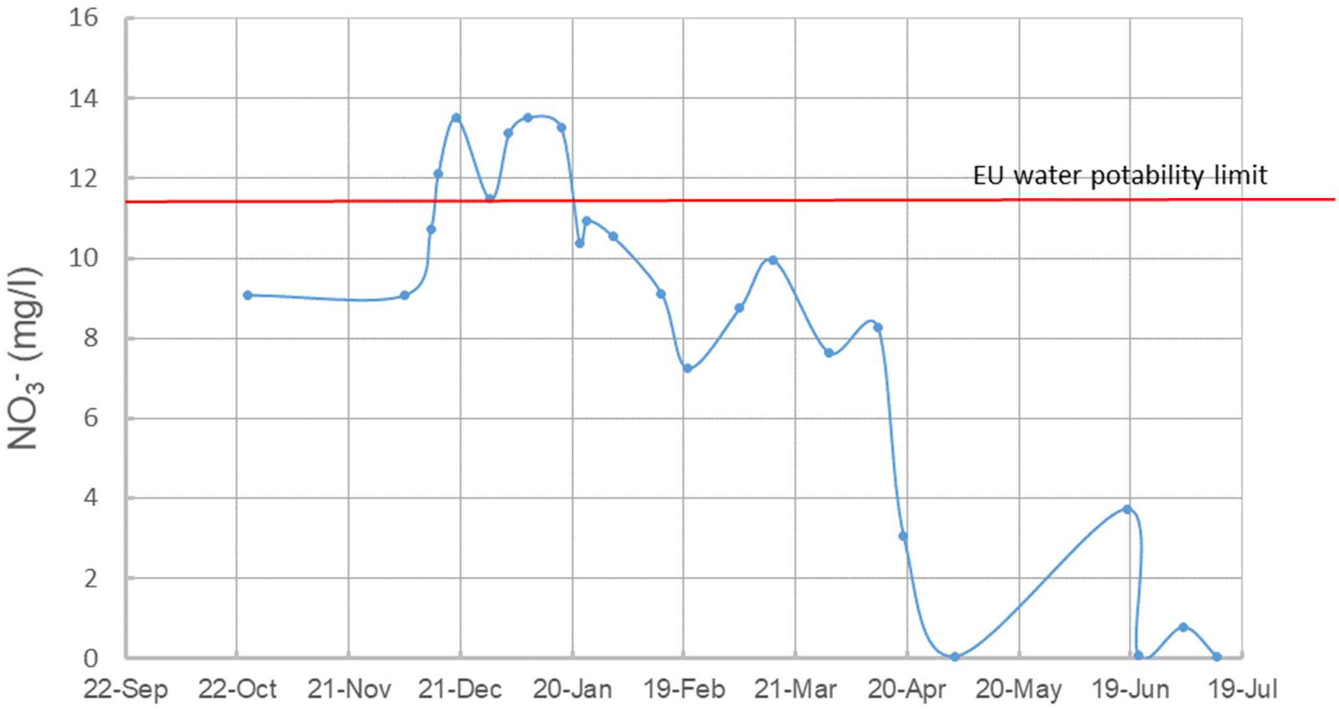


Figure 5. Evolution of the nitrate concentrations in the drained water compared to threshold adopted by the European Union

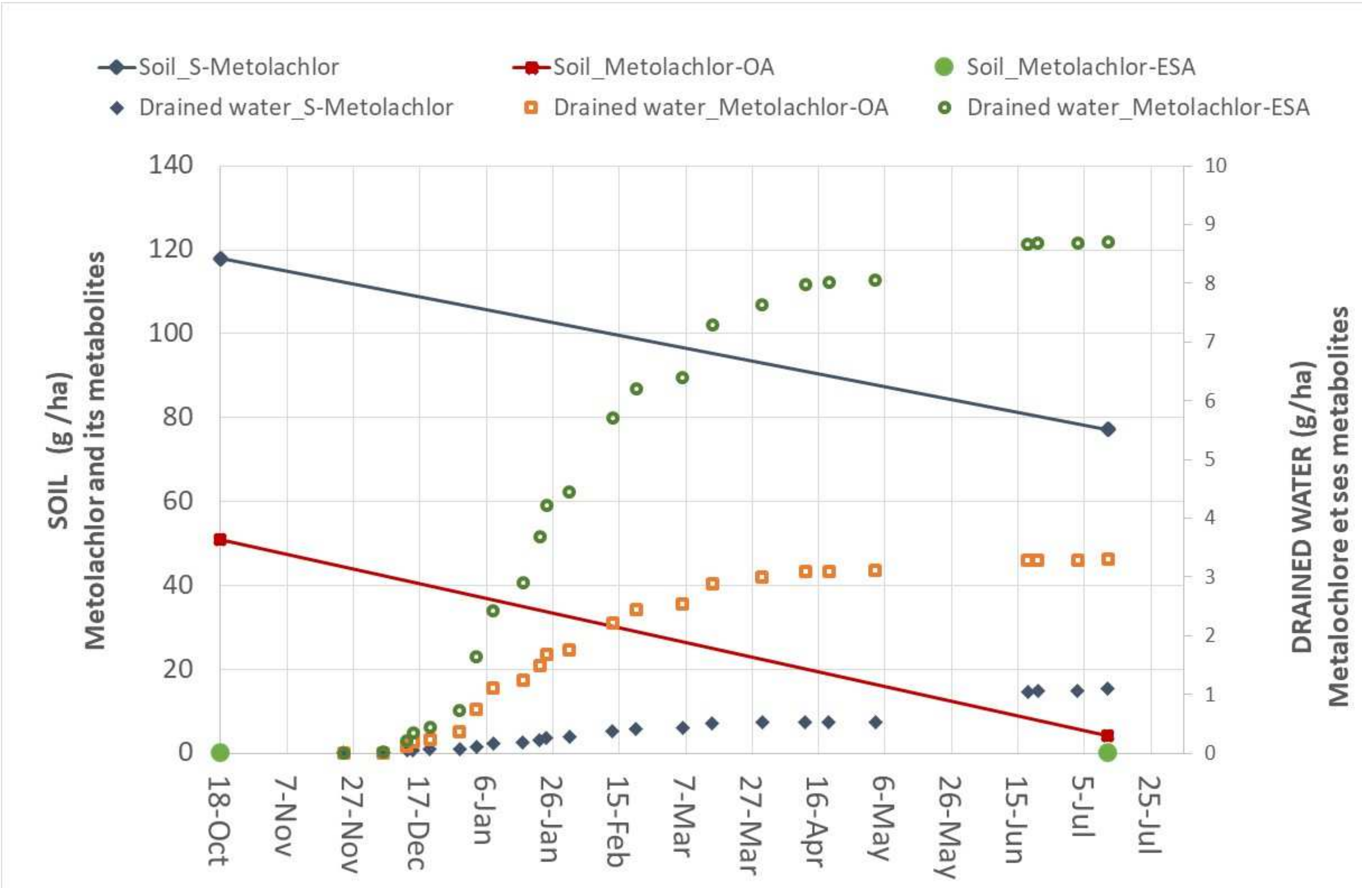


Figure 6. Evolution over time of the amount of S-Metolachlor (cumulative: solid line) and its two metabolites in the soil and drained water

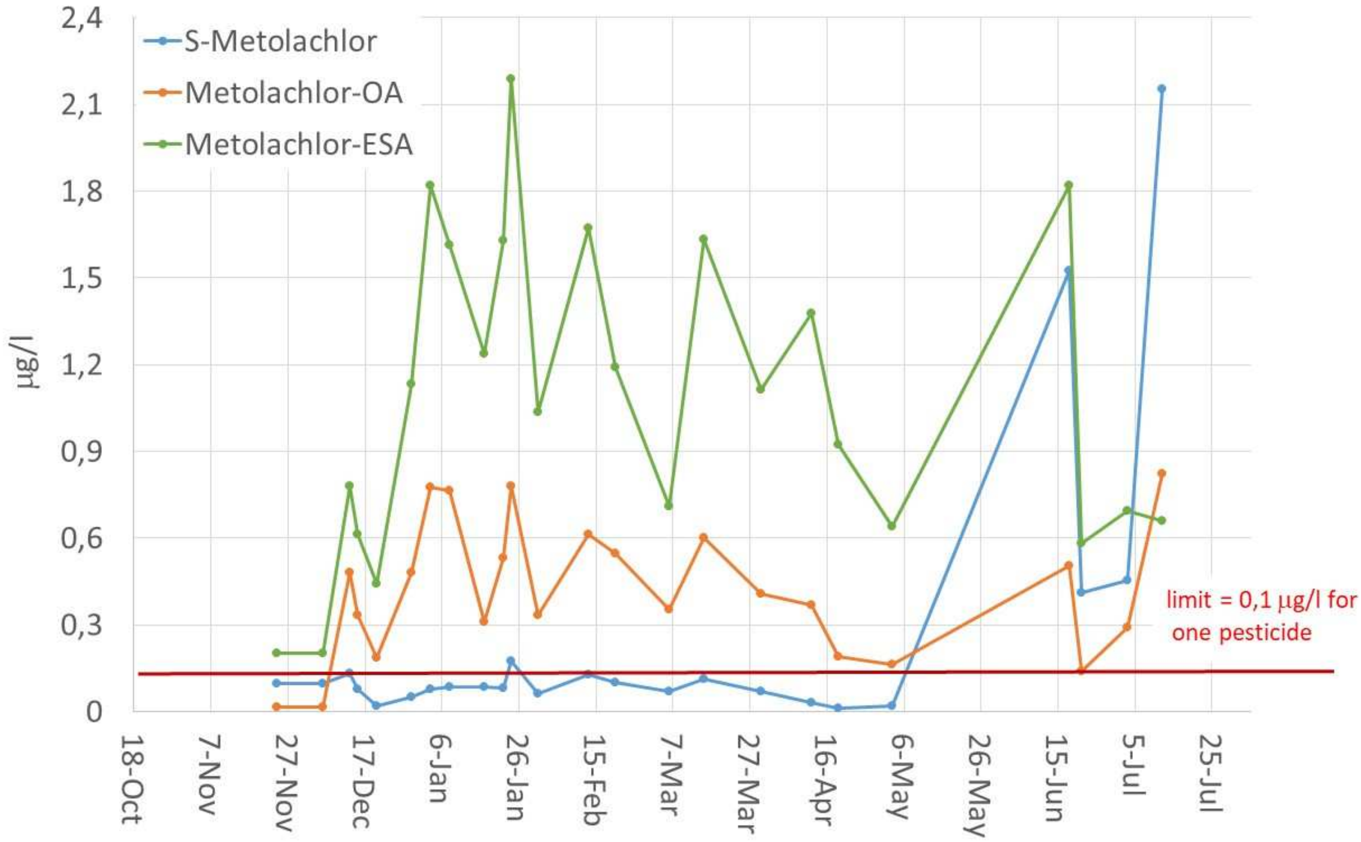


Figure 7. Evolution over time of the concentrations S-Metolachlor and its two metabolites in drained water compared to the threshold adopted by the European union (Farlin et al., 2018)