Method Article

Coupling the water footprint accounting of crops and in-stream monitoring activities at the catchment scale

Ersilia D'Ambrosio[a,b], Anna Maria De Girolamo[b,*], Maria Cristina Rulli[a]

[a] Department of Civil and Environmental Engineering, Politecnico di Milano, Milan, Italy
[b] Water Research Institute, National Research Council, Bari, Italy

A B S T R A C T

In this work, a simple approach for calibrating the water footprint (WF) accounting of crops with in-stream measurements at the catchment scale was developed. The green and blue components of the WF were evaluated by performing a soil-water balance at a 10-day time-interval. The surface runoff was calibrated based on continuous streamflow measurements. Meanwhile, the grey component of the WF related to nitrogen use was quantified by means of the results from the in-stream monitoring activities.

The methodology can be applied to any catchment where soil, land use, weather, agricultural practices, nitrogen balance and stream data are available. This methodological approach can support local authorities in the decision-making process for effective agricultural policy setting and water planning.

- The WF accounting for an agricultural catchment is coupled with surface-water monitoring results
- The green and blue WF are assessed by performing a soil-water balance
- Surface runoff and grey water accounts are based on in-stream monitoring activities

* Corresponding author at: Water Research Institute, National Research Council, 70132, Bari, Italy.
  E-mail address: annamaria.degirolamo@ba.irsa.cnr.it (A.M. De Girolamo).

Specifications Table

Subject area	• Agricultural and Biological Sciences
More specific subject area	Water Footprints assessments
Method name	Calibrating the water footprint accounting of crops with in-stream measurements at catchment-scale
Name and reference of original method	• Water footprint accounting for catchments and river basins. Calculation of the green, blue and grey water footprint of growing a crop or tree - Irrigation schedule option (Hoekstra, A.Y., Chapagain, A.K., Aldaya, M.M., Mekonnen, M.M., 2011. The Water Footprint Assessment Manual. London – Washington DC) • Estimate the leaching-runoff fraction for nitrogen diffuse pollution sources (Franke, N.A., Boyacioglu, H., Hoekstra, A.Y., 2013. Grey water footprint accounting: Tier 1 supporting guidelines. Unesco-IHE, Delft)
Resource availability	- Software: Soil Water Characteristics (SPAW) (ars.usda.gov/research/software) - Software: Baseflow Filter Program (swat.tamu.edu/software/baseflow-filter-program) - Loads tool [1]

Method details

The water footprint

The water footprint (WF) is a relatively new indicator, introduced by Hoekstra and Hung [2] to enable the quantification of water consumption and pollution, and to foster the implementation of more sustainable water-use practices. Galli et al. [3] included the WF in their 'footprint family', together with ecological and carbon footprints, as a suite of indicators useful in tracking human pressures on the planet from different aspects. The WF is a multidimensional indicator, which accounts for both the direct and indirect appropriation of freshwater resources.

WF assessments should be conducted at the river basin scale in the context of integrated water resource management aimed at sustainable development [4–6]. Despite this observation, agricultural WF accountings at the river basin scale are rare, due to the lack of reliable data at this scale, especially for arid and semi-arid regions, because of the high fragmentation of land use and variable adopted management practices [7].

Method objectives

This study aimed to give general guidance on how to perform a WF accounting of crop production at the catchment scale, in order to evaluate the sustainability of agricultural activities by considering both water quantity and quality. In particular, the defined methodologies aimed to: i) gather reliable data on land use and agricultural practices adopted within the catchment; ii) suggest a detailed program of surface-water monitoring, in order to better understand the hydrological and water-quality processes acting in the catchment, especially for arid and semi-arid regions containing temporary rivers[1] [8]; iii) estimate loads when flow and concentration measurements are not continuous and simultaneous; and iv) couple the assessment of the total WF of catchment-scale crops and in-stream monitoring activities. The methodology for calibrating and quantifying nitrogen export coefficients and water balance components useful for WF assessment constitutes the first experimental work in a basin with a temporary river network. The methodology proposed here can support local authorities in the decision-making process for effective agricultural policy setting and water planning, thus fostering implementation of the EU Water Framework Directive [9].

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[1] Temporary rivers are defined as rivers that experience dry periods over the entire water body, or only in parts of it, recorded either every year, or at least twice within five years [8]

Table 1

Manure production, live weight (LW) and TN excretion rates of different animal types.

Animal type	Manure production rates t t LW^{-1} y^{-1}	Live weight Kg LW animal^{-1}	TN excretion rate kg animal^{-1} y^{-1}
Horse	15.0	360.0	24.9
Dairy cattle	26.0	450.0	59.5
Beef cattle	26.0	400.0	33.6
Sheep, goat	15.0	50.0	5.0
Swine	22.0	119.5	13.9
Hen	9.5	1.4	0.3
Poultry	8.0	3.8	0.7
Rabbit	8.0	3.5	0.2

Analysis of agricultural practices

Official data on anthropogenic activities and agricultural management practices adopted in a catchment come from agricultural censuses; however, agronomic data are generally aggregated at different spatial levels (region, province, municipality), and their downscaling needs to be verified through a detailed survey campaign. Indeed, a large difference in the amount of fertiliser used can be found between rural mountainous areas and plains areas devoted to intensive agriculture [10]. Taking into account this difference, local citizens and farmers were interviewed, and the information provided by five owners was selected as being representative of agricultural holdings for land use, cultivation techniques and management practices for the integrated census data. These owners provided information on the type, timing and amount of fertilisers used for each crop, annual crop yields, crop rotation, tillage operations and irrigation supply.

The amount of the total nitrogen (TN) application rate had to be estimated for each crop within the catchment boundaries, including the TN in synthetic fertilisers (N_{SF}), and in animal manure (N_{AF}) if that was used as fertiliser. In this study, the TN from N_{AF} was estimated for each animal type, multiplying the animal-specific TN excretion rates by the live weight of each animal type [11,12] (Table 1). A distinction between indoor and outdoor farming was made. For manure produced by indoor farming, a 27.5% of TN loss during manure handling and storage was considered [13]. Appendix A contains all the acronyms/abbreviations used in this paper.

Surface-water monitoring

Hydrological processes are characterised by high temporal and spatial variability, especially in arid and semi-arid regions with temporary rivers [14,15]. A quantification of pollutants delivered to rivers requires monitoring activities that analyse all streamflow conditions (flood events, normal and low flow) [16–18].

In the case study location (Celone, Apulia, Italy), an automatic sampler (ISCO model 6712FS) with an internal data logger was installed [17] (Fig. 1). The sampler was connected to a flow module (ISCO 750 Area Velocity Flow Module) to measure stream water stage and velocity, which were converted to streamflow using a predefined stage-discharge rating curve. The sampler offers different sets of programming. In particular, two sets were selected: i) a time-space sampling program; and ii) a program that was triggered by water-level changes during the rising limb of the hydrograph, and flow rates during flood recession. With the first standard program, periodic samples were taken at monthly or fortnightly intervals during summer and autumn, and once or twice a week from November to June. For flood events (second program), the time intervals varied from 15 min to 2 h over the rising limb of the hydrograph, and from 2 h to one day over the flood recession. The concentrations of ammonia (N-NH_4), nitrate (N-NO_3), nitrite (N-NO_2), total organic nitrogen (TON) and TN (TN = TON + N-NH_4 + N-NO_3 + N-NO_2) were determined using the APAT-IRSA chemical standard analytical methods [19].

In order to evaluate the contribution of point sources (i.e., wastewater treatment plants discharging into the river system), if present, it was necessary to analyse nitrogen concentrations upstream and downstream from the point-source discharge. In the Celone catchment, wastewater
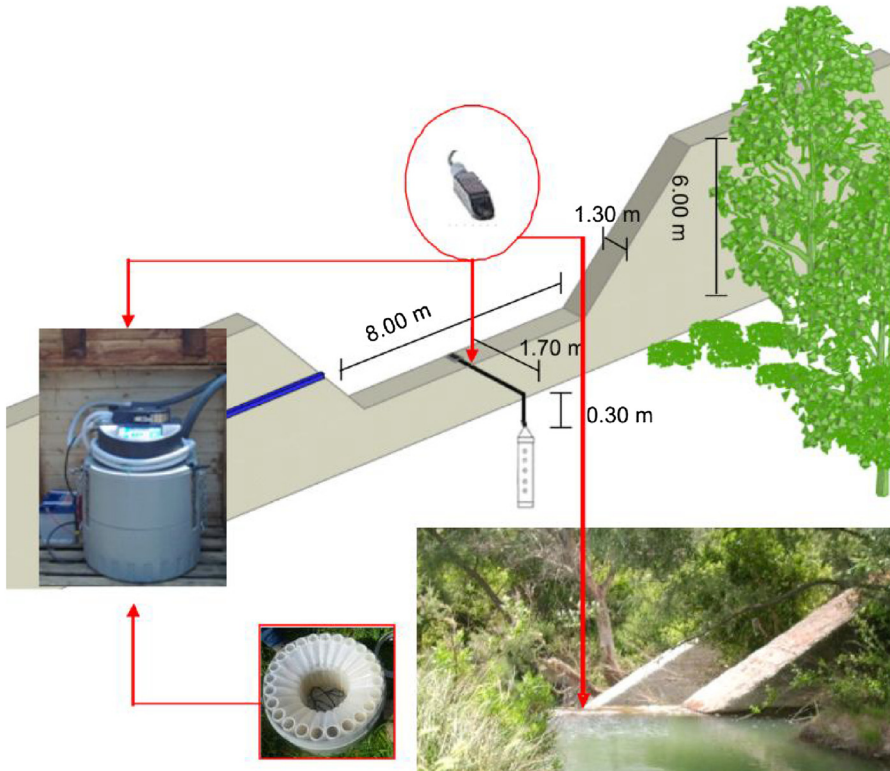
Fig. 1. Automatic sampler installed at the closing section of the Celone catchment.

was treated in three treatment plants (about 3000 inhabitant equivalents) and discharged into the river (Fig. 2).

Detailed descriptions of the instruments and methods used can be found in De Girolamo et al. [10,16,17].

Riverine nitrogen export estimates

Estimating load, when flow and concentration measurements are not continuous and simultaneous, is not an easy task. In recent years, several methodologies have been developed [20–22]. Tan et al. [23] summarised the data requirements and applicability of the different methods. They suggested using averaging methods if no significant relationship between streamflow and nutrient concentration exists. The 'Loads' tool [1] provides monthly and annual load calculations as a result of different methods. The tool requires daily streamflow data (continuous time-series) and discrete daily concentration values.

A preliminary calculation of the daily equivalent concentration was needed for those days during which several samplings were performed (flood events). Eq. (1) was used for the Celone catchment, since the time interval of streamflow measurements was 15 min.

$$DailyL = 0.9 \sum_{i=1}^{96} q_i c_i \qquad (1)$$

, where $DailyL$ is the daily load (kg) passing through the river section (L), qi is measured streamflow (L) at time interval t (1, 2, ... 96), c_i is the measured or linearly-interpolated concentration (mg L^{-1}) at
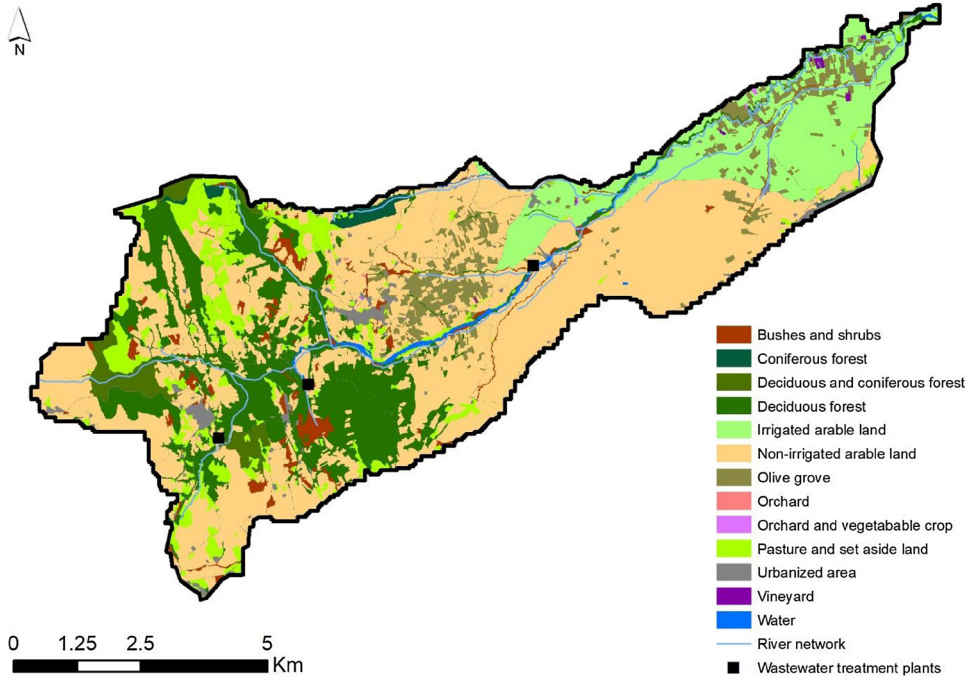
Fig. 2. Land cover map of the Celone catchment (Corine Land Cover – IV Level, 2011).

time t (1, 2, ... 96), 0.9 is the time interval ($15 \times 60 = 900$ s, which includes the conversion factor 1000^{-1}). By dividing *DailyL* by the daily volume, the daily equivalent concentration was obtained.

For the Celone catchment, four methods, using some form of average in the calculation of the loads, we employed. These are: Method 1 – intersample mean concentration (Eq. (2)); Method 2 – intersample mean concentration using mean flow (Eq. (3)); Method 3 – linear interpolation of concentration (Eq. (3)); and Method 4 – concentration power curve fitting (Eq. (4)). We used these methods since the number of samples was high throughout the year (100 or more), and the samples covered all flow conditions (high, normal and low flow) [20–22].

In Method 1, the concentration values were averaged to estimate unsampled days:

$$L = \sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} Q_j \tag{2}$$

, where Cj is the jth sample concentration and Q_j is the jth flow.

Method 2 assumed that the average daily concentration on non-sampled days was determined by a simple linear average of the concentrations from the last sample data and the next sample date. The flow was assumed to be the average flow up to the next sampled concentration value.

$$L = \sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} \overline{Q}_{j+1} \tag{3}$$

, where Cj is the jth sample concentration and $\overline{Q}_{j+1}$ is the average flow to the end of the $j + 1$ period.

Method 3 used Eq. (3), but assumed that the concentration on non-sampled days was determined by linearly interpolating between fortnightly or monthly sampled concentrations.
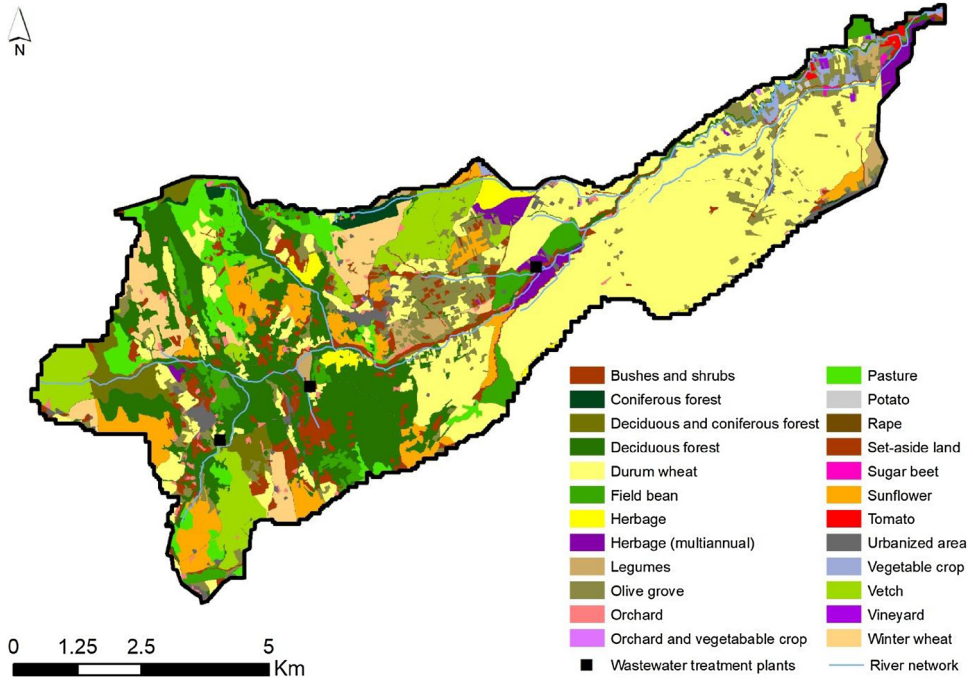
Fig. 3. Celone catchment land cover map reclassified after farmer interviews and field surveys.

Meanwhile, Method 4 used a power function:

$$k \sum_{i=1}^{n} \frac{c_i}{n} \sum_{i=1}^{n} \frac{q_i}{n} = k\overline{c}\,\overline{q} \tag{4}$$

, where c_i is the ith concentration, when it exists, and aq_i^b otherwise, a being a calculated coefficient, q_i is i^{th} sampled discharge (flow), b is the calculated power, $\overline{c}$ is the average of n concentration measurements, $\overline{q}$ is the average of n discharge measurements and k is the number of time intervals in a period.

These methods provided four different values for the monthly and annual loads. The results were similar for the averaging methods (Methods 1, 2, 3; in the case study, being from 280 t y^{-1} and 292 t y^{-1}), whilst Method 4 provided a lower value for load (199 t y^{-1}). Previous studies have demonstrated that power curve methods (Method 4) underestimate high concentrations and overestimate low values [24]. The accuracy of the averaging methods depends on the number of samples and on the time between two successive samples. In temporary streams, data stratification could be applied, based on the hydrological regime, to improve the estimation.

The mean, minimum and maximum annual nitrogen riverine export (N$_{RE,mean}$, N$_{RE,min}$, N$_{RE,max}$) were calculated in order to calibrate the leaching-runoff fractions, and estimate the uncertainty.

Nitrogen input from point sources

When data concerning point sources were missing, nitrogen input waste loads (TN point sources – N$_{PS}$) were estimated by using the following equation:

$$N_{PS} = Q_w\,C_w = Q_r\,C_r - Q_u\,C_u \tag{5}$$

, where Q_u is the upstream flow, Q_w is the wastewater flow rate, Q_r is the flow rate downstream of the source, C_u is the upstream TN concentration, C_w is the concentration of the wastewater and C_r is the
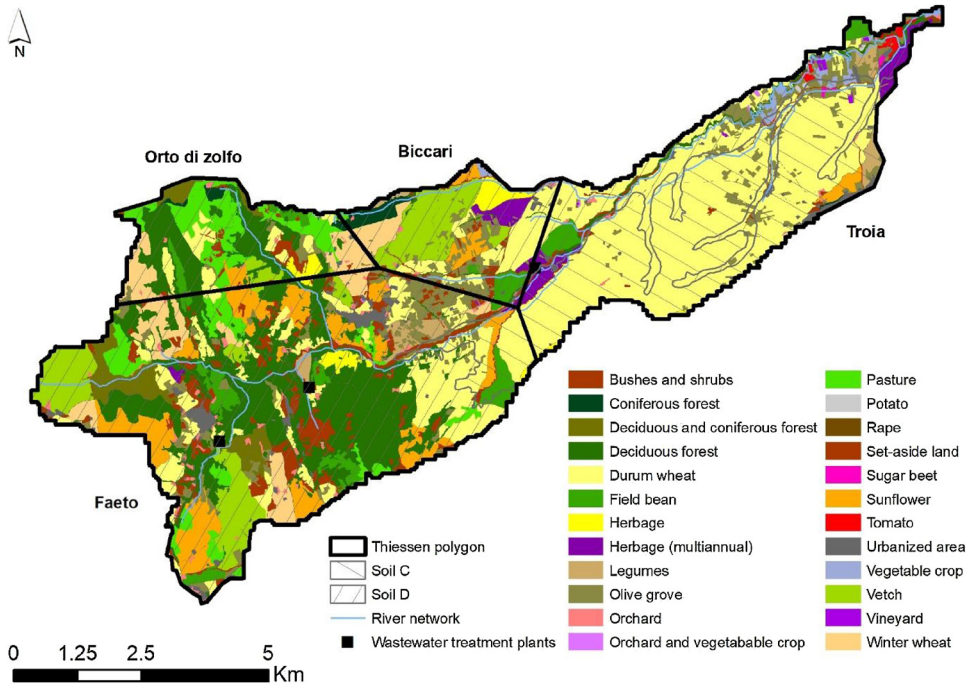
Fig. 4. Land use map, soil map and rainfall zones used for identifying LUSs within the Celone catchment.

concentration downstream. If one sample per month is collected, the flows and concentrations are assumed to be the same throughout the month as on the day of sampling. The equation must be applied to each point source discharging into the river net.

Definition of land-use systems

Land use is the first level of information that is generally derived from a land cover map. In this study, we used the land cover map provided by the local authorities (Corine Land Cover – IV Level, 2011), which was obtained from satellite imagery (www.sit.puglia.it). Since the map has a spatial resolution of 1:100,000, and does not allow distinction among arable land types, it was reclassified by crossing data from agricultural censuses with data from local surveys and field inspections. In particular, the agricultural census provided data on crop areas at a municipal scale. Meanwhile, from local surveys and field inspections, information on crop irrigation was obtained.

Figs. 2 and 3 show the initial land cover map along with the reclassified land use map obtained for the Celone catchment (Puglia Region, SE Italy), respectively. Irrigated and non-irrigated arable lands of the land cover map were divided among crucifers, durum wheat, field bean, herbage, legumes, potato, sugar beet, sunflower, tomato, vegetable crop, vetch and winter wheat, as deduced from municipal agricultural censuses and farmer interviews.

In order to perform a soil-water balance, calibrate the leaching-runoff fraction and finally assess the total WF of catchment-scale crops, the watershed was preliminarily divided into land-use systems (LUSs), defined as areas with similar land use, soil characteristics and precipitation amounts [25,26]. Therefore, land-use maps, soil maps and rainfall zones (Thiessen polygons) can be intersected by means of specific GIS tools. Previously, soil maps had to be reclassified according to hydrological soil groups (i.e., A, B, C, D) [27].

Considering the Celone catchment, in addition to the precipitation gauges present in the catchment, all the gauging stations within a 25 km buffer were included in the analysis. Thus,
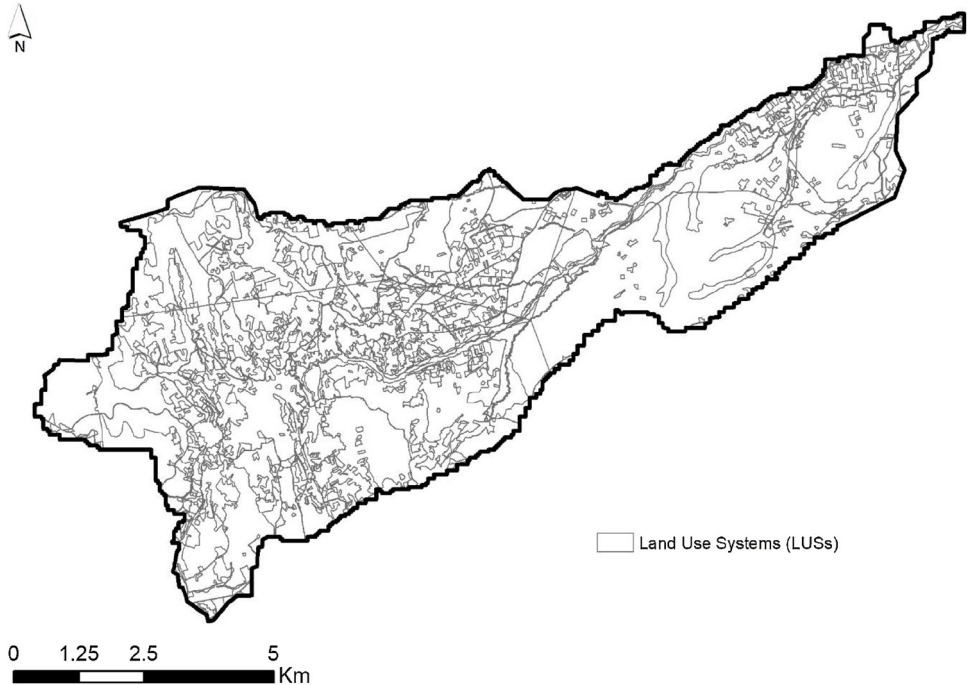
Fig. 5. Land Use Systems (LUSs) within the Celone catchment, 103 identified.

21 precipitation gauges were considered. Four rainfall zones, two hydrological soil groups (C, D) and 24 land-use classes have been distinguished [27] (Fig. 4). Hence, 103 LUSs were identified (Fig. 5).

Accounting of the water footprint

The WF includes different types of water consumption, such as water volume from rainfall, which evapotranspirates (green water), irrigation water volume (blue water) and the water required to assimilate pollution (grey water).

The total WF ($m^3 t^{-1}$) was calculated as the sum of the green (WF_{green}), blue (WF_{blue}) and grey (WF_{grey}) components [28]:

$$WF = WF_{green} + WF_{blue} + WF_{grey} \qquad (6)$$

To perform a complete WF assessment of crop production on a river basin scale, it is necessary to evaluate the WFs associated with each crop growing within the watershed. Hydrological and water quality models can be used for estimating the WF components, although these approaches require specific knowledge about the model and data for their calibration and validation [29].

In this study, an easy approach for estimating the green, blue and grey components of the WF assessment was performed by slightly modifying the calculation framework proposed by Franke et al. [30] and Hoekstra et al. [28] (Fig. 6). The proposed approach does not require specific modelling training.

A calibration procedure aimed at quantifying the nitrogen export coefficients (leaching and runoff fractions) and the water balance components (runoff), by means of observed surface runoff data, measured nitrogen load and nitrogen balance results, was developed.

Fig. 6. WF accounting methodology.

Green water footprint

The WF_{green} was calculated as the ratio of the volume of green water used for crop production (CWU_{green}, m^3 ha^{-1} y^{-1}) to the average annual crop yield, Y (t ha^{-1} y^{-1}) [28]:

$$WF_{green} = \frac{CWU_{green}}{Y} \tag{7}$$

CWU_{green} refers to the part of the precipitation that does not runoff or leach, since it is temporarily stored on top of the soil or vegetation and/or in the soil. This water can evaporate or transpire through plants, and be an important factor in agricultural production, especially in rain-fed croplands [31].

A multitude of different empirical formulae or crop models exist to estimate CWU_{green} in agriculture [28]. In this study, the 'irrigation schedule option' was used, since it is more accurate, and is applicable to both optimal and water-stressed growing conditions. According to this procedure, the CWU_{green} of a crop is assumed to be equal to the crop evapotranspiration under non-standard conditions (also called 'actual', or 'adjusted crop', evapotranspiration), and assuming that the soil does not receive any irrigation ($ET_{c,adj}$):

$$CWU_{green} = ET_{c,adj} = K_c \, ET_0 \, K_s \tag{8}$$

, where K_c is the single crop coefficient (dimensionless), ET_0 is the reference evapotranspiration (mm time^{-1}) and K_s is the stress coefficient (dimensionless).

Calculating evapotranspiration

The computation of $ET_{c,adj}$ is generally done following the methods and assumptions provided by Allen et al. [32]. A time interval of 10 days (10-d) is considered to provide a good representation of hydrological processes [33].

Since K_c varies in time as a function of plant growth stage, 10-d-averaged single crop coefficients ($K_{c,i}$) are calculated for each crop in the catchment from the crop coefficient curves, which are constructed using initial K_c ($K_{c,ini}$), middle K_c ($K_{c,mid}$) and end K_c ($K_{c,end}$). Data concerning crop planting dates and length of cropping season were provided from the above-mentioned interviews with farmers and local dealers.

Referring to the calculation methodology adopted for the ET_0 estimate (mm d^{-1}), the following equation [34] was applied to the temperature gauges, if solar radiation, relative humidity and wind speed data, required by other methods (i.e., the Penman–Monteith equation), were missing in the study area [32,35]:

$$ET_0 = 0.0023 * \frac{RA}{\lambda} * (T_{max} - T_{min})^{0.5} * (T_{mean} + 17.8) \tag{9}$$

, where λ is the latent heat of vapourisation (MJ kg^{-1}), RA is the extraterrestrial solar radiation (MJ m^{-2} d^{-1}) and T_{max}, T_{min} and T_{mean} are the daily maximum, minimum and mean air temperatures (°C), respectively.

Daily λ is obtained by applying the Harrison formula [36]:

$$\lambda = 2.5 - 0.002 * T_{mean} \tag{10}$$

Daily ET_0 values were calculated by applying Eq. (9), then appropriately summing these in order to obtain values on a 10-d basis ($ET_{0,i}$).

Finally, a GIS-based inverse distance weighted method was used in order to spatially interpolate the punctual $ET_{0,i}$ values in the entire watershed, considering a 10-d time-interval [37,38]. For the Celone catchment, in addition to the temperature gauges present in the catchment, all the gauging stations within a 25 km buffer were included in the analysis. Thus, 13 temperature gauges were considered.

After calculating the crop evapotranspiration under standard conditions ($ET_{c,i} = K_{c,i} ET_{0,i}$), K_s was evaluated as follows [32]:

$$\begin{cases} K_{s,i} = \dfrac{TAW - D_{r,i-1}}{TAW - RAW} & D_{r,i-1} > RAW \\ K_{s,i} = 1 & D_{r,i-1} \leq RAW \end{cases} \tag{11}$$

, where TAW (mm) is the total available water in the root zone, RAW (mm) is the readily available water in the root zone and $D_{r,i-1}$ (mm) is the root zone depletion at the start of the 10-d period considered. Formulae (12) and (13) were used to assess TAW and RAW values, respectively:

$$TAW = 1000(\theta_{FC} - \theta_{WP})Z_r \tag{12}$$

$$RAW = p\,TAW \tag{13}$$

, where θ_{FC} is the water content at field capacity (m^3 m^{-3}), θ_{WP} is the water content at wilting point (m^3 m^{-3}), Z_r is the rooting depth (m) and p is the soil-water depletion fraction for no stress, the values of which have been tabulated by Allen et al. [32].

The θ_{FC} and θ_{WP} depend on the type of soil, and average values can be estimated with the software Soil Water Characteristics, implemented by the USDA Agricultural Research Service. Z_r is estimated considering the lowest value between the depth of the soil layers in the watershed and that reported for various crops by Allen et al. [32].
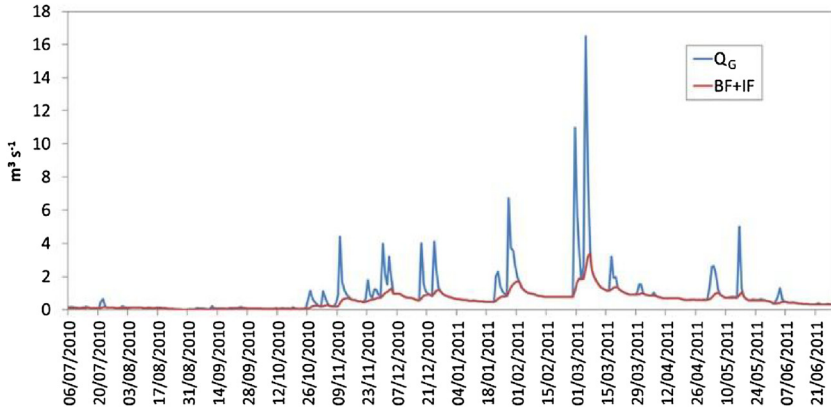
Fig. 7. Measured daily streamflow (Q_G) and sum of baseflow (*BF*) and interflow (*IF*) in the Celone catchment closing section.

Soil-water balance computation

Lastly, a water balance computation for the root zone was implemented on a 10-d basis, in order to estimate root zone depletion at the end of the 10-d period ($D_{r,i}$, mm). Hence, a GIS model with a resolution of 20 m was developed. According to Allen et al. [32], the incoming (irrigation, rainfall) and outgoing (runoff, deep percolation, evapotranspiration) water flux into the crop root zone have to be assessed. Water transferred horizontally by subsurface flow in or out of the root zone is ignored. Moreover, if the groundwater table is more than ∼1 m below the bottom of the root zone, the amount of water transported upwards by capillary action can be assumed to be zero.

Therefore, the following equation for the water balance was used:

$$D_{r,i} = D_{r,i-1} - P_{n,i} + RO_i - I_i + ET_{c,adj,i} + DP_i \tag{14}$$

, where $P_{n,i}$ (mm) is the net precipitation, RO_i (mm) is the runoff from the soil surface, I_i (mm) is the irrigation depth, $ET_{c,adj,i}$ (mm) is the actual crop evapotranspiration and DP_i (mm) is the water loss out of the root zone by deep percolation. $D_{r,i}$ and $D_{r,i-1}$ can assume values between 0 and *TAW*.

The $P_{n,i}$ is determined as follows:

$$P_{n,i} = P_i - 0.2ET_{0,i} \tag{15}$$

, where P_i (mm) is the total precipitation amount. Thiessen polygons are built and rainfall zones are distinguished [25,26]. $ET_{c,adj,i}$ is determined according to Eq. (8), whilst Eq. (16) is used for the determination of DP_i:

$$\begin{cases} DP_i = P_i - RO_i + I_i - ET_{c\,adj,i} - D_{r,i-1} > 0 & D_{r,i} = 0 \\ DP_i = 0 & 0 \le D_{r,i} \le TAW \end{cases} \tag{16}$$

The I_i values are set to zero for irrigated crops, both in Eqs. (14) and (16), in order to estimate CWU_{green} [28,39].

RO_i was estimated using the Soil Conservation Service Curve Number (SCS-CN) method [27], which is one of the most commonly-used models due to its simplicity and the requirement for few data [40,41]. This model is used to predict the depth of surface runoff (*RO*, mm) for a given rainfall event, and can be expressed as follows:

$$\begin{cases} RO = \dfrac{(P - 0.2S)^2}{P + 0.8S} & P > 0.2S \\ RO = 0 & P \le 0.2S \end{cases} \tag{17}$$

, where S is the potential maximum retention or infiltration (mm) and P is the total storm rainfall (mm). S was evaluated using the following equation:

$$S = 25.4\left(\frac{1000}{CN} - 10\right)$$
(18)

, where CN is the curve number (dimensionless) that ranges from 1 (minimum runoff) to 100 (maximum runoff). This parameter was determined and tabulated based on hydrological soil group and soil cover type, treatment and hydrological condition [42]. The tabulated values (CN II) refer to the average antecedent moisture condition (AMC II). The AMC definition depends on the total 5-d antecedent rainfall, and the season category (dormant or growing) that is defined from daily average temperatures [43]. Different CN conversion formulae, from AMC II, to dry AMC (AMC I – CN I) and wet AMC (AMC III – CN III), have been proposed [44]. For this case study, the Hawkins et al. [45] CN conversion formulae were used.

In summary, CN II tabulated values were associated with each LUS identified in the basin; AMC was evaluated for the identified rainfall zones and, where necessary, CN I and CN III were calculated. After that, Eqs. (17) and (18) were applied, and the runoff associated with single precipitation events was estimated for each LUS. Considering a 10-d time interval, the runoff was appropriately added, and the preliminary RO_i (mm) was obtained. This latter value was then modified, following the calibration procedure described below, and based on the continuous flow measurements at the gauge.

The water balance for the root zone (Eq. (14)) was initiated in the first 10-d period of a really wet month. Therefore, it was assumed that, in that month, the root zone was near field capacity and, hence, $D_{r,i-1} = 0$, $K_{s,i} = 1$ and $ET_{c,adj,i} = ET_{c,i}$ [46].

Calibrating curve numbers

Daily mean baseflow (BF, m³ s⁻¹), daily mean interflow (IF, m³ s⁻¹) and total daily mean wastewater discharge (WW, m³ s⁻¹) were subtracted from the mean daily streamflow recorded at the gauge (Q_G, m³ s⁻¹), as follows:

$$SF_G = Q_G - BF - IF - WW$$
(19)

, where SF_G (m³ s⁻¹) is the estimated daily mean stormflow, Q_G is obtained from the continuous measurement of flow, and BF and IF can be assessed by means of the baseflow filter program (swat. tamu.edu/software/baseflow-filter-program). Fig. 7 shows the measured streamflow, the sum of the daily mean baseflow and the daily mean interflow in the Celone catchment closing section.

Volumes of surface runoff ($SF_{G,i}$, m³) were estimated throughout the study period, considering a 10-d time step (i). Based on these values, the CNs associated with each LUS were recalculated, so that the sum (m³) of RO_i ($\sum RO_i$, Eq. (17)) was equal to $SF_{G,i}$ (Eq. (19), the target function). To do this, a spreadsheet was specifically created, and the target function was set. Finally, calibrated CN values were used to estimate the RO_i (mm), required for the soil-water balance.

Results for the Celone catchment can be found in D'Ambrosio et al. [47].

Blue water footprint

The WF_{blue} refers to the consumption of groundwater and/or surface-water resources that are utilised in crop production (i.e., irrigation water) [28]. In other words, it is the amount of groundwater and/or surface water that does not return to the source in the form of return flow, and is different from water withdrawn for irrigation, insofar as this water is returned to where it came from.

The WF_{blue} (m³ t⁻¹) was calculated by dividing the total volume of blue water used – CWU_{blue} (m³ ha⁻¹ y⁻¹) – by the quantity of the annual production – Y (t ha⁻¹ y⁻¹):

$$WF_{blue} = \frac{CWU_{blue}}{Y}$$
(20)

The CWU_{blue} (mm time⁻¹) was calculated by performing another soil-water balance (Eq. (9)) on a 10-d basis, and irrigation (I_i) was considered, as proposed by Hoekstra et al. [28] and applied by Mekonnen

and Hoekstra [39], de Miguel et al. [48], Zhuo et al. [46] and Rulli and D'Odorico [49]. I_i values could be deduced from the above-mentioned interviews. The following equation was then used:

$$CWU_{blue} = ET_{c, adj}^{I \neq 0} - ET_{c,adj} \tag{21}$$

, where $ET_{c,adj}^{I \neq 0}$ is the adjusted crop evapotranspiration, estimated by means of the same procedure applied for $ET_{c,adj}$ evaluation (Eq. (8)), but considering also I_i in Eqs. (14) and (16). In the case of rain-fed crops, CWU_{blue} is zero.

Grey water footprint

The WF_{grey} refers to the volume of water needed to dilute a load of pollutants discharged into the natural water body in such a way that the quality of the receiving water system is not compromised, with respect to specific quality standards and natural background concentrations [6,28]. In this study, the WF_{grey} related to nitrogen use was quantified, thus excluding the effects of other nutrients and fertilisers. Hence, the intensity of water pollution caused by agricultural activities and, in particular, by the TN application rate, was measured.

The WF_{grey} (m^3 t^{-1}) was calculated by dividing the dilution water requirement, CWU_{grey} (m^3 ha^{-1} y^{-1}), by the crop yield, Y (t ha^{-1} y^{-1}) [28]:

$$WF_{grey} = \frac{CWU_{grey}}{Y} \tag{22}$$

The CWU_{grey} (mm y^{-1}) was calculated by multiplying the fraction of TN that leaches or runs off (leaching-runoff fraction – α) by the TN application rate (AR, kg ha^{-1} y^{-1}), and dividing this by the difference between the maximum (C_{max}) and natural (C_{nat}) concentration (mg l^{-1}) of TN in freshwater:

$$CWU_{grey} = \frac{\alpha * AR}{C_{max} - C_{nat}} \tag{23}$$

The AR was estimated for each LUS, based on the above-mentioned interviews. Meanwhile, a calibration procedure was defined in this study in order to divide α between leaching (α_L) and runoff (α_R), as follows. Finally, CWU_{grey} was estimated by summing the values associated with runoff ($CWU_{grey,R}$) and leaching ($CWU_{grey,L}$).

Calibrating the runoff and leaching nitrogen fraction

In most of the previous studies, α has been set at a constant value of 10% [39,46,50] or 7% [51]. In contrast to the use of a static α throughout the watershed, the procedure suggested by Franke et al. [30], and applied by Brueck and Lammel [52], Munro et al. [53] and Gil et al. [54], was preliminarily used in this study. This approach considers that α depends on potential factors – (j) – which are atmospheric input (TN deposition), soil type (texture and natural drainage), climate (precipitation) and agricultural practice (TN fixation, application rate, plant uptake and management practice). The α values were calculated for each LUS (k), using the following equation:

$$\alpha_k = \alpha_{min} + \left[\frac{\sum_j s_{j,k} * w_{j,k}}{\sum_j w_{j,k}} \right] * (\alpha_{max} - \alpha_{min}) \tag{24}$$

, where α_{min} is the minimum leaching runoff fraction (0.01), α_{max} is the maximum leaching runoff fraction (0.25), $s_{j,k}$ is the score for the above-mentioned potential factor, j, associated with the LUS k, and $w_{j,k}$ is the weight of the factor j associated with k.

Franke et al. [30] provided specific criteria used to score (s) and weight (w) all the different influencing factors (j). Unlike in previous studies, the procedure suggested by Franke et al. [30] was slightly modified in this study, and α_k was divided between leaching ($\alpha_{L,k}$) and runoff ($\alpha_{R,k}$). Then, a zero weight ($w_{j,k}$) was assigned to factors specifically related to runoff (i.e., texture and natural drainage relevant to runoff) and leaching (i.e., texture and natural drainage relevant to leaching), respectively.

At the watershed closing section, TN runoff (R, kg y^{-1}) and TN in soil and leaching (L, kg y^{-1}) were estimated using Eqs. (25) and (26):

$$R = \sum_{k=1}^{n} \alpha_{R,k} AR_k A_k \tag{25}$$

$$L = \sum_{k=1}^{n} \alpha_{L,k} AR_k A_k \tag{26}$$

, where n is the number of LUSs identified within the watershed, $\alpha_{R,k}$ and $\alpha_{L,k}$ are the runoff and leaching fraction associated with the LUS k, AR_k (kg ha^{-1} y^{-1}) is the application rate associated with the LUS k and A_k (ha) is the surface of the LUS k.

Following this, $\alpha_{L,k}$ and $\alpha_{R,k}$ were recalculated, following a calibration procedure based on the field measurements [55]. Thus, R (Eq. (25)) and L (Eq. (26)) were equalised to TN runoff (R_M, Eq. (27)) and TN in soil and leaching (L_M, Eq. (28)) estimated from field measurements. Hence, the values of $\alpha_{R,k}$ and $\alpha_{L,k}$ were multiplied by an appropriate constant factor. A spreadsheet was specifically created in order to set the target function and obtain the constant factor.

$$R_M = N_{RE} - N_{BF} - N_{AD} - N_{PS} - N_{NAT} \tag{27}$$

$$L_M = \Delta - (N_{RE} - N_{PS} - N_{NAT}) - N_{BF,\ soil\ D} - N_{AD,\ soil\ D} \tag{28}$$

, where N_{RE} (kg y^{-1}) is the annual TN riverine export, N_{BF} (kg y^{-1}) is the TN biological fixation, N_{AD} (kg y^{-1}) is the TN atmospheric deposition, N_{PS} (kg y^{-1}) is the TN in wastewater, N_{NAT} (kg y^{-1}) is the TN naturally present in the river, Δ (kg y^{-1}) is the difference between TN input (N_{SF}, N_{AF}, N_{BF}, N_{AD}) and output (crop uptake – N_{CU}, NH$_3$ volatilisation – N_V and denitrification in soil – N_D) in the study area. Moreover, $N_{BF,soil\ D}$ and $N_{AD,soil\ D}$ are N_{BF} and N_{AD}, respectively, associated with soil of hydrological group D, where infiltration does not occur.

N_{NAT} was assessed by multiplying C_{nat} for the total discharge, Q_{TOT} (m^3 y^{-1}), measured at the gauge, and N_{PS} was determined, as described in the section above. Meanwhile, Δ was obtained from a nitrogen balance [10,56,57]. In particular, for the Celone catchment, N_{BF} (64,891 kg y^{-1}), N_{AD} (39,744 kg y^{-1}) and Δ (306,397 kg y^{-1}) values are reported in De Girolamo et al. [10].

The values of L_M were set to be greater than zero. If the uncertainty in the WF_{grey} estimate related to α variability was assessed, the mean, minimum and maximum annual nitrogen riverine export ($N_{RE,\ mean}$, $N_{RE,min}$, $N_{RE,max}$) were considered as N_{RE} in Eqs. (27) and (28).

Results for the Celone catchment can be found in D'Ambrosio et al. [47].

Maximum and natural TN concentrations in surface and groundwater

Regarding the C_{max} value in Eq. (23), despite that the idea of measuring water pollution in terms of the amount of water needed to dilute pollutants can be traced back to Falkenmark and Lindh [58], and was continued by Postel et al. [59] and Chapagain et al. [50], still today there are uncertainties related to the standardisation of water-quality standards that should be used for a consistent WF_{grey} assessment, taking into account the diverse ambient water quality and aquatic ecosystems, as well as the presence of several pollutants in water-bodies [6]. Generally, WF_{grey} assessments have used drinking-water standards. Regardless of the fact that this value is referred to a surface-water or groundwater body, the US EPA (10 mg N-NO$_3$ l^{-1}) or the European Union/World Health Organization (50 mg NO$_3$ l^{-1}, i.e., 11.3 mg N-NO$_3$ l^{-1}) nitrogen standards for drinking-water are the most commonly used water-quality standards [39,50,51,60–62]. Also, 50 mg NO$_3$ l^{-1} is the maximum concentration permitted by the EU Nitrate Directive in groundwater [63]. In the literature, only a few studies have used ambient water-quality standards [46,64,65]. In Italy, the Decree of the Ministry of the Environment n. 260/2010 [66] identifies, among various physicochemical factors, the threshold

concentrations of NH_4, NO_3 and NO_2 that are required to support a functioning ecosystem. Concerning groundwater, a good chemical status is reached if the concentrations of NH_4, NO_3 and NO_2 are lower than $0.5 \, mg \, l^{-1}$ (i.e., $0.4 \, mg \, N\text{-}NH_4 \, l^{-1}$), $50 \, mg \, l^{-1}$ and $0.5 \, mg \, l^{-1}$ (i.e., $0.1 \, mg \, N\text{-}NO_2 \, l^{-1}$), respectively. Meanwhile, the threshold values associated with the good water-quality status of a surface-water body for $N\text{-}NH_4$ and $N\text{-}NO_3$ are 0.06 and $1.2 \, mg \, l^{-1}$, respectively. Currently, Italian legislation does not provide ambient quality thresholds for TN in either surface water or groundwater. Following Liu et al. [6], the TN ambient water-quality standard (good) adopted for Celone catchment surface water is $3 \, mg \, l^{-1}$. Meanwhile, the standard adopted for groundwater is $4.6 \, mg \, l^{-1}$ [67].

Regarding the C_{nat} value in Eq. (23), many previous studies have considered this value to be equal to zero, due to a lack of data [49,50,61,63,68]; however, such an assumption leads to an underestimation of CWU_{grey} because C_{nat} is generally higher than zero. For the Celone catchment, since local data are not available, the C_{nat} of TN was set $0.4 \, mg \, N \, l^{-1}$ in both river water and groundwater, as recommended by Franke et al. [30], and used by Mekonnen and Hoekstra [69] and Liu et al. [6].

Limitations of the study

The main limitations of the procedure adopted in this study for the calibration of runoff and the nitrogen leaching runoff fraction are [47]:

- the SCS-CN method was used beyond its original scope, since it was not applied considering a single storm event, but the sum of storm events that happened in a 10-d period. In addition, small events that produce no runoff were not excluded. These limitations can lead to an overestimation of CN II values;
- the limited time period analysed (1 year), with wetter than average conditions, could have greatly influenced the outcomes, especially the WF_{grey} that could have resulted in being higher than average. An average over multiple years would be more appropriate for representing the WF and the general status of water scarcity;
- the discretisation of the watershed into LUSs (based on land use, soil type and Thiessen polygons) adopted in this study leaves out local factors, such as slope, rainfall intensity and river distance. The latter factors influence hydrological processes and the leaching and runoff fraction, hence, neglecting them could lead to an overestimate or underestimate of these variables;
- the high fragmentation of land use, and the different management practices adopted within the catchment, makes the assignment of actual agricultural practices to each field impossible, hence, the agricultural practices used in the calculations (i.e., fertiliser amount, crop yield) can be affected by certain uncertainty;
- TN accumulation and degradation processes in the receiving water-bodies were neglected in the TN load calculations, whilst biochemical processes can be relevant, especially in temporary rivers;
- the in-stream monitoring of TN concentration program (i.e., number of samples, time between two successive samples, hydrological conditions), as well as the method used for estimating load, have a great influence on load estimation that results in a large uncertainty in the runoff and leaching nitrogen fraction estimation. A standard procedure is needed for fixing Cmax and Cnat. Maximum allowable concentrations fixed on standards for drinking-water lead to an underestimation of grey water, as well as a natural background fixed as equal to zero.

Region for providing climatic data. Thanks are also due to several local citizens who provided information and data about the management practices and to the agronomist Dr. Giuseppe De Vita for supervising these data. Lastly, the authors are indebted to four anonymous Reviewers for their scientific comments and recommendations.

Appendix A. Glossary

Abbreviation	Description	Unit of measure
TN	Total Nitrogen	–
A_k	Surface of the Land Use System k	ha
AR	TN application rate	kg ha^{-1} y^{-1}
AR_k	TN application rate associated with the Land Use System k	kg ha^{-1} y^{-1}
BF	Daily mean baseflow	m^3 s^{-1}
C_{max}	Maximum concentration of TN in the water bodies	mg l^{-1}
CN	Curve number	dimensionless
C_{nat}	Natural concentration of TN in the water bodies	mg l^{-1}
CWU_{blue}	Blue crop water use	m^3 ha^{-1} y^{-1} (mm time^{-1})
CWU_{green}	Green crop water use	m^3 ha^{-1} y^{-1} (mm time^{-1})
CWU_{grey}	Dilution water requirement	m^3 ha^{-1} y^{-1} (mm time^{-1})
$CWU_{grey,L}$	Dilution water requirement (leaching)	m^3 ha^{-1} y^{-1} (mm time^{-1})
$CWU_{grey,R}$	Dilution water requirement (runoff)	m^3 ha^{-1} y^{-1} (mm time^{-1})
DP_i	Water loss out of the root zone by deep percolation at the end of the 10-d period	mm (10-d)$^{-1}$
$D_{r,i}$	Root zone depletion at the end of the 10-d period	mm (10-d)$^{-1}$
$D_{r,i-1}$	Root zone depletion at the start of the 10-d period	mm (10-d)$^{-1}$
ET_0	Reference evapotranspiration	mm time^{-1}
$ET_{0,i}$	10-d reference evapotranspiration	mm (10-d)$^{-1}$
$ET_{c,adj}$	Actual (or adjusted) crop evapotranspiration assuming that the soil does not receive any irrigation	mm time^{-1}
$ET_{c,adj,i}$	Actual crop evapotranspiration at the end of the 10-d period assuming that the soil does not receive any irrigation	mm (10-d)$^{-1}$
$ET_{c,adj,i}^{I\neq0}$	Actual crop evapotranspiration at the end of the 10-d period considering irrigation	mm (10-d)$^{-1}$
$ET_{c,i}$	10-d crop evapotranspiration under standard conditions	mm (10-d)$^{-1}$
IF	Daily mean interflow	m^3 s^{-1}
I_i	Irrigation depth at the end of the 10-d period	mm (10-d)$^{-1}$
K_c	Single crop coefficient	dimensionless
$K_{c,end}$	End single crop coefficient	dimensionless
$K_{c,i}$	10-d average single crop coefficient	dimensionless
$K_{c,ini}$	Initial single crop coefficient	dimensionless
$K_{c,mid}$	Middle single crop coefficient	dimensionless
K_s	Stress coefficient	dimensionless
$K_{s,i}$	10-d stress coefficient	dimensionless
L	TN in soil and leaching calculated with Eq. (26)	kg y^{-1}
L_M	TN in soil and leaching estimated for the study area with Eq. (28)	kg y^{-1}
N_{AD}	TN atmospheric deposition	kg y^{-1}
$N_{AD,soil\ D}$	TN atmospheric deposition associated with soil D	kg y^{-1}
N_{AF}	TN in animal manure	kg y-1
N_{BF}	TN biological fixation	kg y^{-1}
$N_{BF,soil\ D}$	TN biological fixation associated with soil D	kg y^{-1}
N_{CU}	TN crop uptake	kg y^{-1}
N_{NAT}	TN naturally present in the river	kg y^{-1}
N_{PS}	TN point sources	kg y^{-1}
N_{RE}	TN riverine export ($N_{RE,mean}$; $N_{RE,min}$; $N_{RE,max}$)	kg y^{-1}
$N_{RE,max}$	Annual maximum TN riverine export	kg y^{-1}
$N_{RE,mean}$	Annual mean TN riverine export	kg y^{-1}
$N_{RE,min}$	Annual minimum nitrogen riverine export	kg y^{-1}
N_{SF}	TN in synthetic fertilisers	kg y^{-1}
N_V	NH$_3$ volatilisation	kg y^{-1}
p	Soil water depletion fraction for no stress	dimensionless

(*Continued*)

Abbreviation	Description	Unit of measure
P	Total storm rainfall	mm time^{-1}
P_i	Total precipitation amount at the end of the 10-d period	mm (10-d)$^{-1}$
$P_{n,i}$	Net precipitation at the end of the 10-d period	mm (10-d)$^{-1}$
Q_G	Mean daily streamflow recorded at the gauge	m^3 s^{-1}
Q_{TOT}	Total discharge measured at the gauge	m^3 y^{-1}
R	TN runoff calculated at the watershed closing section with Eq. (25)	kg y^{-1}
RA	Daily extraterrestrial solar radiation	MJ m^{-2} d^{-1}
RAW	Readily available water in the root zone	mm
R_M	TN runoff estimated at the watershed closing section with Eq. (27)	kg y^{-1}
RO_i	Runoff from the soil surface at the end of the 10-d period	mm
S	Potential maximum retention or infiltration	mm
SF_G	Estimated daily mean stormflow	m^3 s^{-1}
$SF_{G,i}$	Volumes of surface runoff at the end of the 10-d period	m^3 (10-d)$^{-1}$
$s_{j,k}$	Score for the potential factor that influence leaching and runoff (j) associated with the Land Use System k	dimensionless
TAW	total available water in the root zone	mm
T_{max}	Daily maximum air temperature	°C
T_{mean}	Daily mean air temperatures	°C
T_{min}	Daily minimum air temperature	°C
WF	Total water footprint	m^3 t^{-1}
WF_{blue}	Blue water footprint	m^3 t^{-1}
WF_{green}	Green water footprint	m^3 t^{-1}
WF_{grey}	Grey water footprint	m^3 t^{-1}
$w_{j,k}$	Weight of the potential factor that influence TN leaching and runoff (j) associated with the Land Use System k	dimensionless
WW	Total daily mean wastewater treatment plant (WWTP) discharge	m^3 s^{-1}
Y	Average annual crop yield produced	t ha^{-1} y^{-1}
Z_r	Rooting depth	m
α	Leaching-runoff fraction	dimensionless
α_k	α values calculated for each Land Use System k	dimensionless
α_L	Leaching fraction	dimensionless
$\alpha_{L,k}$	Leaching fraction associated with the Land Use System k	dimensionless
α_{max}	Maximum leaching-runoff fraction	dimensionless
α_{min}	Minimum leaching-runoff fraction	dimensionless
α_R	Runoff fraction	dimensionless
$\alpha_{R,k}$	Runoff fraction associated with the Land Use System k	dimensionless
Δ	Difference between TN input and TN output	kg y^{-1}
θ_{FC}	Water content at field capacity	m^3 m^{-3}
θ_{WP}	Water content at wilting point	m^3 m^{-3}
λ	Latent heat of vaporisation	MJ kg^{-1}

Appendix B. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mex.2018.10.003.

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