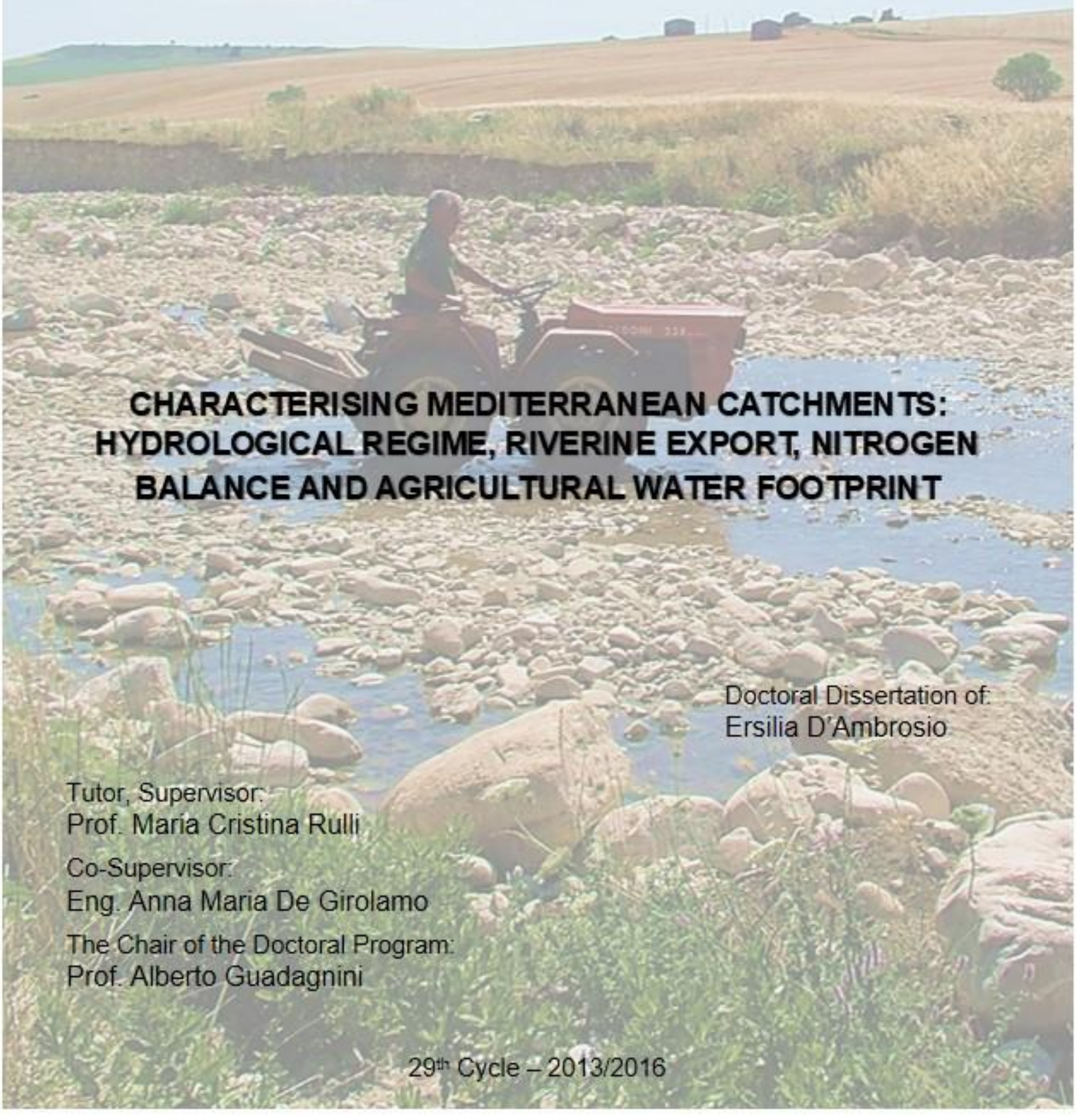
POLITECNICO DI MILANO

DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

DOCTORAL PROGRAMME IN ENVIRONMENTAL AND INFRASTRUCTURE ENGINEERING



CHARACTERISING MEDITERRANEAN CATCHMENTS: HYDROLOGICAL REGIME, RIVERINE EXPORT, NITROGEN BALANCE AND AGRICULTURAL WATER FOOTPRINT

Doctoral Dissertation of:
Ersilia D'Ambrosio

Tutor, Supervisor:
Prof. Maria Cristina Rulli

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"The most beautiful human deed, is to be useful to others."

Sophocles

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ABSTRACT

Agriculture has been identified as one of the main cause of water consumption and degradation, due to the large use of fertilizers and pesticides. In a catchment, nitrogen (TN) export from terrestrial ecosystems to rivers is controlled by hydrological regimes and TN balance. Hence, before assessing the sustainability of agriculture and defining how the current use of water resources can affect their quantity and quality is important to characterise the hydrological regime, the anthropogenic TN input and the riverine export.

In such a context, this research was designed to develop a simple approach for classify the stream regime, to quantify the soil system TN budget and the riverine export, and to assess the sustainability of agriculture through a full agricultural Water Footprint Assessment at a catchment scale in Mediterranean Region characterised by temporary streams.

A set of 37 Hydrological Indicators (HIs) were examined in three Mediterranean catchments (Carapelle, Candelaro and Cervaro) and two HIs (flow permanence, MF and flow predictability, SD6) were identified as the best indicators for classify streams regime in Mediterranean watershed. The TN balance and the riverine export were quantified in the Celone watershed (South-East, Italy) through several survey campaigns, continuous measures of streamflow and discrete determinations of concentrations recorded from July 2010 to June 2011. Major N inputs derived from fertilizers and animal manure correspond to 68 and 12 kg N ha^{-1} yr^{-1}, respectively. TN fluxes in stream during flood events accounted for about 60% of the annual loading.

The riverine TN export (from diffuse sources) was estimated to be about 34.5 kg ha^{-1} yr^{-1}. On a yearly basis, the difference between N inputs and outputs including riverine export (from diffuse sources) was estimated in about 8.1 kg N ha^{-1} yr^{-1} for the whole watershed area. This amount partly accumulates in soils in different N forms and the remaining part, mainly in form of nitrate, percolates through unsaturated soil towards groundwater. Meanwhile, results for the study period (July 2010 – June 2011) show the total WF to be 79.9 million m^3 y^{-1}, subdivided into 30.3% green water, 0.5% blue water and 69.2% grey water, thus highlighting the importance of grey water in the estimate of agricultural water use. Moreover, the results show the grey WF estimates to be highly sensitive both to leaching and runoff fractions, and applied water standards, and affected by large uncertainty. The sustainability assessment of present water consumption, subdivided into the three WF components, indicates sustainable use of green water, fluctuating sustainability of blue water resources, depending on the season and the environmental flow requirement, and unsustainable grey water production and water pollution level for the Celone River.

The methodologies and the results presented in this research constitutes a useful tool for ecologists and water resource managers in order to classify the 'river type', understand TN loss dynamics and execute more functional water management and land use planning. Hence, this research constitutes a helpful analysis for the Water Framework Directive implementation process in Mediterranean watershed with a temporary river system.

Keywords: Temporary river, Mediterranean Basin, Hydrological Indices, Point and Non Point Sources, Load estimation, Nitrogen balance, Water footprint, Integrated river basin management

SUMMARY

1 INTRODUCTION

Water is a core component of human well-being, and is essential for a thriving economy and healthy-functioning ecosystem (D'Ambrosio et al., 2018; Vigerstol and Aukema, 2011). Increasing human population and anthropogenic activities, unsustainable development and economic growth, place pressure on water quality and availability (Lamastra et al., 2014; Vitousek et al., 1997a). Since the world's freshwater stock corresponds to only 2.5% of the total global water reserve, and freshwater is considered a scarce natural resource, the need to optimise its utilisation in all human activities is promoting a worldwide effort to instigate more efficient water usage (Gleick, 1993; Stathatou et al., 2012). Indeed, over-exploitation and pollution of freshwater presents a massive threat to sustaining future water demand, and to economic development (Brueck and Lammel, 2016).

Agriculture has been identified as one of the main causes of water consumption and degradation, due to the use of large volumes of water for irrigation, and of pesticides and fertilisers in order to achieve an increase in food and non-food productions (Chouchane et al., 2015; De Girolamo et al., 2012a; Lovarelli et al., 2016; Rulli and D'Odorico, 2013; Ventura et al., 2008; Willaarts et al., 2012). In Italy, water drawn by agriculture accounts for about 44.07% of the total national water withdrawal (FAO, 2016). Furthermore, the use of fertilisers, exceeding plant demand, has dramatically increased the amount of nutrients, such as nitrogen compounds (N) entering the terrestrial biosphere (Bennett et al., 2001).

Indeed, a large N input-output imbalance occurs in agricultural lands and nutrient surpluses are generally found in all industrialized countries (Organisation for Economic Co-operation and Development, 2008). In tropical areas, Vitousek et al. (2009) found that more than 80% of nitrogen fertilizer applied in agriculture did not make it into crops.

The N surplus accumulates in soils and is transported to the rivers and groundwater through surface runoff and leaching (Capri et al., 2009; Lionetto et al., 2016; Sacchi et al., 2013; Wick et al., 2012). As consequence, high concentrations of N can be found in freshwater, which put human and ecosystem health at risk. Indeed, exposure to high levels of nitrates increases the risk of diseases like stomach cancers, methaemoglobinemia, birth defects and spontaneous abortions and causes toxic effects on livestock, fish, shellfish, and smaller organisms that live in water, causing biodiversity loss (Boyer et al., 2006; Galloway and Cowling, 2002; Merrington et al., 2002; Vitousek et al., 1997b; Weyer et al., 2001).

The European Union (EU) recognizes the intense environmental pressures on water bodies and the resulting deterioration in their quality. With the Nitrates Directive (EC Directive 91/676/EEC) and Water Framework Directive (WFD) (EC Directive 2000/60/EC) the EU requires UE Member States to control pollution and improve the ecological status of fresh water resources.

In such a context, the implementation of properly methodologies and tools for the definition of the ecological status and for the management is nowadays a major prerequisite for the sustainable development of Mediterranean river basins through the protection of river ecosystems and the preservation of the services that they provide (Datry et al., 2014; Nikolaidis et al., 2013; Prat et al., 2014). Indeed, the WFD, that considers all streams in the same way, mostly ignore temporary streams since it was developed from the perspective of permanent running waters (Logan and Furse, 2002).

Differently from permanent rivers, temporary rivers are characterised by irregular and harsh streamflow fluctuations and periodically cease to flow (D'Ambrosio et al., 2017). The flow pattern in these rivers during the year, known as the hydrological regime, is characterised by seasonal variations and extreme low or zero flow. This pattern is determined largely by watershed size and shape, climate, geology, soil type, topography and land cover (Arthington et al., 2014). The spatial and temporal distribution of flow and its volume provide the geomorphic forces necessary to create and maintain stream river habitats (Poff et al., 1997). However, streamflow influences not only ecosystem processes but several other processes including channel formation, floodplain and flood processes, groundwater and surface water interactions, sediment regime, nutrient delivery, water quality and ecological status (Arthington, 2014; Bonada et al., 2007; Buffagni et al., 2009; De Girolamo et al., 2012b).

Moreover, data and information concerning Mediterranean basins are generally poor (Oueslati et al., 2015). As example, in Italy, only water level measurements and a few (3–4) sampling concentrations per year are generally available. Unfortunately, this sampling strategy is inadequate to evaluate pollutant loads and water quality, not only with direct methods but also with eco-hydrological models. In particular, for small catchments in the Mediterranean area, characterized by high temporal and spatial variability of hydrological processes, a quantification of pollutants delivered to rivers requires monitoring activities that analyse the flood events, in addition to the normal and low flow conditions (Bianchi et al., 2004; De Girolamo et al., 2012a; De Girolamo et al. 2015; Fox, 2005; Zonta et al., 2005). In fact, it is well known that during floods, pollutant concentrations have a wide range of variability (Eyre and Pont, 2003; Royer et al., 2006) and the flood loads constitute the majority of the total annual pollutant loads especially in temporary streams (De Girolamo et al., 2015b; Obermann et al., 2007). Meanwhile, the intermittency of streamflow in temporary channels, which has a great influence on the dynamics of pollutant, sediment and aquatic ecosystems, needs an analysis of dry periods (Larned et al., 2010; Prat et al., 2014). In fact, the latter are punctuated by water pulses, which have influence on sediment and pollutant delivery (Arce et al., 2013; Welter and Fisher, 2016).

Monitoring activity covering flood events is a difficult task, especially in temporary river systems where flash events are quite frequent. It requires an expensive equipment composed of an automatic sampler connected with a flow measurements module, but limited financial resources often do not allow to install this instrument. Moreover, the river bank instability that characterizes the temporary river systems and the vandalism acts make the choice of location to install the instruments very difficult. For all these difficulties, few data are available covering long time periods (Gentile et al., 2010). Thus, due to the peculiarities of temporary river systems, the implementation of the WFD has been delayed indicating the need for specific tools that address the special character of such water bodies (Nikolaidis et al., 2013). Considering the timetable of the WFD, the development of new methods is desirable because of the pending review and update of the second River Basin Management Plan (2021). In particular, proper methodology to determine the hydrological status and specific actions in River Management Plans, aiming to prevent water quality and quantity deterioration (such as load estimate, N budget and Water Footprint assessment), constitute one of the challenges for water management related Directives in Mediterranean catchments (Nikolaidis et al., 2013).

Hydrological status evaluation

The WFD requires the evaluation of hydro-morphological aspects as supporting elements in classifying the ecological status of a water body (Annex V, WFD). Hence, the hydrological status (HS), which is the deviation of the actual hydrological regime (impacted conditions) from its natural state, have to be assessed (D'Ambrosio et al., 2017). In addition, the WFD requires the classification of water bodies [1] into 'river types' and the individuation of reference sites for each river type.

Currently, methodologies for evaluating HS constitute a challenge for hydrologists and ecologists especially for temporary rivers. Furthermore, the classification defined by the WFD (Annex II, WFD), which is based on abiotic factors, is inadequate for heterogeneous water districts such as the Mediterranean basins. Indeed, for these rivers, Munné and Prat (2004) propose a more detailed classification based mainly on geology and flow regime.

A multitude of different methods exist to characterise streamflow. Thus, a large number of hydrological indicators (HIs) have been developed to describe hydrological regimes (Richter et al., 1996). HIs are also used for the eco-hydrological classification of rivers (Gallart et al., 2012; Snelder et al., 2005), environmental flow assessments, hydrological alteration evaluations (Arthington, 2014; Mackay et al., 2014; Poff et al., 2010) and for flow regime characterisation in agricultural or urban rivers (Hamel et al., 2015). HIs are generally grouped into five classes focusing on the description of magnitude, frequency, duration, timing and the rate of change of hydrological conditions. These characteristics can be used to describe the entire range of flow regimes and specific hydrological phenomena such as floods or low flows.

Stream ecologists and hydrologists have to face the difficult task of choosing from a large number of available HIs. Indeed, a limited subset of HIs are able to adequately describe the main aspects of flow regime minimising the redundancy. HIs are calculated on the basis of daily or monthly streamflow recorded in a river section over a long time period. Hydrologists suggest using at least 20 years of recorded data for the calculations (Richter et al., 1997). This can be a limitation, especially in the Mediterranean Basin, where several catchments are ungauged and measured flow data are often unavailable (De Girolamo et al., 2015a). Hence, a methodology is needed to evaluate HIs in the absence of measured streamflow data which must be based on free and accessible catchment physical characteristics.

Load estimate

Moreover, EU Directives require a quantification of water quality status as above mentioned. In such a context, several methodologies have been developed to estimate diffuse nutrient loads extending from the simplified methods, based just on unit loads or export coefficients of various diffuse pollutants, to more complex models, such as Bayesian Network (Arnold et al., 1998; Marcé et al., 2004; De Girolamo et al., 2017a; Nash et al., 2010; Novotny, 2002; Schoumans et

1 The Directive requires Member States to identify 'water bodies' as part of the analysis of the characteristics of the river basin districts. The analysis must be reviewed and where necessary, updated by 22 December 2013 and then every six years

al., 2009). Indeed, the export is influenced by several factors such as hydrology, climate, agricultural practices, slope and soil properties.
Ecohydrological models generally are able to reproduce quality aspects in normal-flow conditions, while their performance in simulating episodic phenomena may be affected by an high uncertainty, especially if measured data for calibrating these events are not available (De Girolamo and Lo Porto, 2012; Nikolaidis and Tzoraki, 2007; Ribarova et al., 2008). Direct estimation methods (Letcher et al., 2002; Littlewood et al., 1998; Quilbé et al., 2006) based on streamflow and concentration measurements are generally preferred (De Girolamo et al., 2017b).

TN budget assessment
The awareness of the fact that an N imbalance is not sustainable in the long-term has given an impulse to comprehensive studies on N dynamics in farming systems (Thayalakumaran et al., 2016), in large and rural catchments (Balestrini et al., 2013; Neal and Heathwaite, 2005), and on N budget calculations (Oenema et al., 2003; Soana et al., 2011; Ventura et al., 2008).
Although in the last decades several studies have been focused on the dynamics, the cycle and balance of N, literature dealing with N budget in river basins under Mediterranean conditions is scarse (De Girolamo et al., 2017a; Lassaletta et al., 2012; Romero et al., 2016).
The lack of data (input and output of N), the variability of physical characteristics of environment and the very fractioned land use may lead to a large uncertainty in N input and output estimations.

Water Footprint assessment
In order to determine how the current use of water resources can affect their availability in the future, and to safeguard their quantity and quality, it is important to study and measure the sustainability of agricultural activities. A multitude of effective and workable indicators has been developed, in order to measure water consumption, such as the Water Stress Index, Sustainability Index, Critical Ratio, Water Footprint (WF), Water Poverty Index, etc. (Pedro-Monzonís et al., 2015; Vollmer et al., 2016; Zeng et al., 2013).
The WF is a relatively new indicator, introduced by Hoekstra and Hung (2002), to enable quantification of water consumption and pollution, and to foster implementation of more sustainable water-use practices. Galli et al. (2012) 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. Furthermore, since the ISO 14046 norm was adopted (ISO, 2014), the WF has become the main international reference for evaluating the sustainability of water use (Pellicer-Martínez and Martínez-Paz, 2016b). The WF is a multidimensional indicator of water use, which accounts for both direct and indirect appropriation of freshwater resources. It includes different types of water consumption, such as water volume from rainfall, evaporated (green) water, irrigation water volume (blue water), and the water required to assimilate pollution (grey water). A full WF assessment consists of four distinct stages, as established by the Water Footprint Network (Hoekstra et al., 2011). The four-step approach includes: i) goals and scope setting; ii) WF accounting; iii) WF sustainability analysis; and iv) if the WF is not sustainable, response formulation, in order to achieve sustainability.
Since the river basin is the common spatial unit in integrated water resource management, the WF assessment should be conducted at this scale (Zeng et al., 2012; Zhi et al., 2015; Liu et al., 2017). Despite this observation, full agricultural WF assessments, on the river-basin scale, are

rare, due to the lack of statistical data at this scale, especially for arid and semi-arid regions, with temporary rivers, whose hydrological processes are characterised by a high temporal and spatial variability (Skoulikidis et al., 2017), and whose management is particularly complex (Nikolaidis et al., 2013). In fact, a detailed and expensive program of surface-water monitoring is required for this type of river, in order to better understand all the processes acting in the catchment. Limited financial resources generally restrain these monitoring activities and, therefore, few measurements are available (De Girolamo et al., 2017a; De Girolamo et al. 2017b; De Girolamo et al. 2015a). Moreover, there are no methodological approaches, or case studies, in the literature for a complete accounting of the WF (Pellicer-Martínez and Martínez-Paz, 2016a), and the concept of grey water is still at an early stage (Zeng et al., 2013).

2 CONTENTS

This work reports an analysis of N pollution in a Mediterranean catchment with a temporary river system, integrated by a surface water resource use assessment, which will be useful for functional water management and long-term land use planning. Four topics were developed having in mind the practicality of the proposed methodologies, which are easy to use by technicians and water resources managers. In this context:

1) new approaches to characterise and classify the hydrological regime of gauged and ungauged temporary streams by means of HIs were defined;
2) the temporal variability of N loads at the basin outlet was studied considering different flow conditions;
3) the N balance in a basin with a limited data availability was evaluated;
4) a complete WF assessment of crop production at river basin scale was performed.

In particular, the specific objectives of the present work were to:

1a. identify a set of non-redundant HIs which describe the critical characteristics of the study area river regime;
1b. describe the relationship between HIs and catchment characteristics through the use of a regression model based on readily available catchment features;
1c. classify the river reaches on their temporariness degree using proper HIs;
2. quantify the export of nitrates from the catchment to the river on annual and monthly basis, and during flood events, using quality and quantity data coming from monitoring activities carried out in a river section;
3. assess the N budget by using data from local farmers' interviews, national agricultural censuses, literature and direct measurements of riverine N loads;
4a. assess the green and blue WFs by performing a soil-water balance test at a 10-day time interval;
4b. quantify the grey WF related to nitrogen use, by means of in-stream monitoring activities, carried out from July 2010 to June 2011;
4c. evaluate blue and green water scarcity and the water pollution level;
4d. identify possible strategies to improve the sustainability of water and land use in countries where water is scarce.

These objectives aim to improve the general understanding of temporary rivers in Mediterranean regions. In an attempt to close the gap between the hydrologists and the water quality community, which frequently characterize studies at the catchment scale, this work discusses the importance of hydrology-controlled transport and links hydrological and water quality dynamics. The methodologies proposed could be applied to any Mediterranean catchment as well, if water quality and quantity measurement are available. The analysed shortcomings could support local authorities in the decision making process for effective agricultural policy setting and water planning, fostering the implementation of the Water Framework Directive (WFD) (Directive 2000/60/EC, 2000).

Two different study areas located in South-Est Italy (i.e. Candelaro – Carapelle - Cervaro watersheds for the first topic and Celone watershed for the rest three) and representative of Mediterranean regions, in terms of climate, land cover, management practices and data availability, were analysed.

In this work the following articles were joined in order to have an overall view of the main issues addressed during the PhD:

- Ersilia D'Ambrosio, Anna Maria De Girolamo, Emanuele Barca, Pierina Ielpo, Maria Cristina Rulli. Characterising the hydrological regime of an ungauged temporary river system: a case study. Environmental Science and Pollution Research (2017), 24(16): 13950–13966;
- Anna Maria De Girolamo, Ersilia D'Ambrosio, Giuseppe Pappagallo, Maria Cristina Rulli, Antonio Lo Porto. Nitrate concentrations and source identification in a Mediterranean river system. Rendiconti Fisici Accademia Lincei (2017), 28: 291–301;
- Anna Maria De Girolamo, Raffaella Balestrini, Ersilia D'Ambrosio, Giuseppe Pappagallo, Elisa Soana, Antonio Lo Porto. Antropogenic input of nitrogen and riverine export from a Mediterranean catchment. The Celone, a temporary river case study. Agricultural Water Management (2017), 187: 190-199;
- Ersilia D'Ambrosio, Anna Maria De Girolamo, Maria Cristina Rulli. Assessing sustainability of agriculture through water footprint analysis and in-stream monitoring activities. Submitted to Journal of Cleaner Production (December 2017);
- Ersilia D'Ambrosio, Anna Maria De Girolamo, Maria Cristina Rulli. Coupling the water footprint assessment of crops and in-stream monitoring activities at catchment-scale. Submitted to MethodsX (December 2017).

3 MATERIALS AND METHODS

3.1 HYDROLOGICAL REGIME CHARACTERIZATION

3.1.1 STREAMFLOW DATA

Streamflow data are fundamental to describing the river hydrological regime and its variations (D'Ambrosio et al., 2017a). In this study, streamflow data were sourced from the 'Hydrological Annals' of the Puglia Region (http://www.protezionecivile.puglia.it/centro-funzionale/analisielaborazione-dati/annali-idrologici-parte-ii).

To account for natural climatic variability, the literature suggests that at least 20 years of daily flow data are necessary to characterise flow variability adequately (Huh et al., 2005; Ritcher at al. 1997). Thus, only stations with at least 20 years of complete daily flow data for the period 1965-1996 were used in the analysis. Unfortunately, more recent daily flow data was unavailable because after 1996, the number of working gauging stations in the Puglia region reduced due to regional financial pressures.

In the Candelaro river catchment, eight gauging stations were found to be compliant with the above requirements. Only one gauging station was found to be compliant in each of the Carapelle and Cervaro river catchments (Fig. 5). The rivers at the analysed stations had low or moderately impacted flow regimes in the study period, mainly due to water abstractions or by wastewater treatment plants discharging sewage water into the river network. As the gauging stations had different years of missing data, it was impossible to analyse flow data over a specific and common time period. Moreover, some station records had relatively minor gaps ranging from several days to a maximum of 4-5 months, mainly in spring and summer (April to September). These gaps occurred either because flow had fallen below the instrument minimum, or the instrument was removed for maintenance during the period when the river network was dry.

Data analysis showed that it was not possible to exclude all the years with missing data, otherwise 20 years of daily flow data (necessary to adequately characterise flow variability) would be not have been available for several stations. Hence two different strategies were adopted to allow for missing data during the wet (from November to April) and the dry (from May to October) seasons. Years containing rainy season gaps were excluded from the analysis, as these gaps would lead to inaccuracies in the determination of HIs (Moliere et al., 2009).

Conversely, years with gaps occurring during periods of low or no flow were not excluded a priori. They were compared with the daily precipitation registered at the nearest meteorological station. If precipitation occurred during the dry season gap, the related year was excluded. Otherwise, if precipitation was not recorded, the missing flow values were estimated by linear interpolation across gap boundaries (Kennard et al., 2010; Olden et al., 2012).

As the number of gauging stations was limited, a second data set of streamflow data for multiple regression analysis was used to make the analysis more robust. This dataset is constituted by simulated daily streamflow from 1990-2009. In De Girolamo et al. (2015b), there is a detailed description of the SWAT model applied to the study area. Table 1 shows all the gauging station characteristics and Fig. 5 shows their location. The stepwise regression is able to overcome the correlated data issues among the catchment features and the model inputs.

Table 1: Gauging station characteristics: location, catchment area (A), elevation (E), data availability within the study period (1965–1996); m is for measured data; s is for simulated data (D'Ambrosio et al, 2017a)

ID	Station name	Basin*	A (km^2)	E (m a.s.l.)	Flow data years	Number of years	% of zero flow record	Qmean ($m^3 s^{-1}$)
m1	S.Maria a Ponte Lucera - Torremaggiore	Can	52.68	93.45	1965-1996	21	33.3%	0.17
m2	Triolo a Ponte Lucera - Torremaggiore	Can	57.23	113.77	1965-1991	23	33.0%	0.22
m3	Salsola a Ponte Foggia - S.Severo	Can	433.30	42.01	1965-1996	31	8.7%	1.24
m4	Casanova a Ponte Lucera - Motta	Can	55.35	180	1965-1996	22	28.1%	0.18
m5	Salsola a Casanova	Can	41.49	186.31	1965-1990	23	21.5%	0.15
m6	Celone a Ponte Foggia - S.Severo	Can	214.70	64.14	1965-1995	26	37.2%	0.69
m7	Vulgano a Ponte Troia - Lucera	Can	95.43	173.49	1965-1993	26	42.1%	0.32
m8	Celone a S.Vincenzo	Can	84.01	192.63	1965-1996	27	37.9%	0.49
m9	Cervaro ad Incoronata	Cer	660.85	57.31	1970-1996	20	16.6%	2.72
m10	Carapelle a Carapelle	Car	720.47	58	1970-1996	20	17.9%	2.26
s1	Canale Ferrante	Can	36.76	53.38	1990-2009	20	75.2%	0.05
s2	Triolo valle	Can	142.86	53.45	1990-2009	20	41.4%	0.48
s3	Rio il Canaletto	Can	40.15	61.8	1990-2009	20	85.5%	0.06
s4	Triolo monte	Can	97.08	61.95	1990-2009	20	38.7%	0.42
s5	Fiumara di Motta Montecorvino	Can	37.67	157.9	1990-2009	20	41.5%	0.24
s6	Affluente Torrente Vulgano	Can	35.56	67.95	1990-2009	20	85.9%	0.04
s7	Torrente Vulgano	Can	36.36	241.3	1990-2009	20	34.3%	0.19

* Can is for Candelaro, Cer is for Cervaro and Car is for Carapelle catchment

3.1.2 HYDROLOGICAL INDICES

Numerous hydrological metrics have been developed in order to characterise hydrological regimes and their degree of alteration (Colwell, 1974; D'Ambrosio et al., 2017a; Ritcher et al,. 1996). In this study 37 HIs were examined (Table 2).

Table 2: Significance description of analysed HIs. The HIs are grouped into five groups, describing ecologically relevant components of the hydrologic regime such as magnitude (group 1), duration (group 2), timing (group 3), frequency (group 4) and rate of changes (group 5) (D'Ambrosio et al., 2017a)

Group	Code	Name	Description
1	MAAN	Mean annual flow	Average annual flow
	MAJ	January mean flow	Average January flow
	MAF	February mean flow	Average February flow
	MAMar	March mean flow	Average March flow
	MAAP	April mean flow	Average April flow
	MAM	May mean flow	Average May flow
	MAJN	June mean flow	Average June flow
	MAJL	July mean flow	Average July flow
	MAAG	August mean flow	Average August flow
	MAS	September mean flow	Average September flow
	MAO	October mean flow	Average October flow
	MAN	November mean flow	Average November flow
	MAD	December mean flow	Average December flow
2	DL1	Annual minima, 1-day minimum	Magnitude of minimum annual flow of 1 day duration
	DL2	Annual minima, 3-day minimum	Magnitude of minimum annual flow of 3 day duration
	DL3	Annual minima, 7-day minimum	Magnitude of minimum annual flow of 7 day duration
	DL4	Annual minima, 30-day minimum	Magnitude of minimum annual flow of 30 day duration
	DL5	Annual minima, 90-day minimum	Magnitude of minimum annual flow of 90 day duration
	DH1	Annual maxima, 1-day mean	Magnitude of maximum annual flow of 1 day duration
	DH2	Annual maxima, 3-day mean	Magnitude of maximum annual flow of 3 day duration
	DH3	Annual maxima, 7-day mean	Magnitude of maximum annual flow of 7 day duration
	DH4	Annual maxima, 30-day mean	Magnitude of maximum annual flow of 30 day duration
	DH5	Annual maxima, 90-day mean	Magnitude of maximum annual flow of 90 day duration
	DL6	Number of zero days	Mean annual number of days having zero daily flow
	ML1	Base flow index	7-day minimum flow divided by mean flow for year
3	TH1	Date of maximum	Julian date of annual maximum
	TL1	Date of minimum	Julian date of annual minimum
4	DH6	High pulse duration	Mean or Median duration of high pulses
	DL7	Low pulse duration	Mean or Median duration of low pulses

Group	Code	Name	Description
	FH1	High pulse count	Number of high pulses within each year
	FL1	Low pulse count	Number of low pulses within each year
5	FI_RB	Richards-Baker Flashiness Index	FI_RB is defined by the following equation: $FI\_RB = \frac{\sum_{i=1}^{n} \lvert q_{i-1} - q_i \rvert}{\sum_{i=1}^{n} q_i}$ where i is the day number and q_i and q_{i-1} are the discharges on day i and day i-1, respectively
	RA1	Rise rate	Median of all positive differences between consecutive daily values
	RA2	Fall rate	Median of all negative differences between consecutive daily values
	RA3	Number of reversals	Number of hydrologic reversals
	MF	Flow permanence	MF is calculated dividing by 12 the long-term average annual relative number of months with flow
	SD6	Predictability	SD6 is defined by the following equation: $SD6 = 1 - \left(\sum_{1}^{6} Fd_i / \sum_{1}^{6} Fd_j \right)$ where Fd_i represents the multi-annual frequencies of 0-flow months for the contiguous 6 wetter months of the year and Fd_j represents the multi-annual frequencies of 0-flow months for the remaining 6 drier months

The indices were split into five groups, describing ecologically relevant components of the hydrologic regime such as magnitude of monthly water conditions (group 1 – n=13), magnitude and duration of annual extreme water conditions (group 2 – n=12), timing of annual extreme water conditions (group 3 – n=2), frequency and duration of high and low pulses (group 4 – n=4) and rate and frequency of water condition changes (group 5 – n=6) (Ritcher et al., 1996; Poff et al., 1997). All hydrological metrics were calculated using the Indicators of Hydrologic Alteration (IHA) software package (The Nature Conservancy, 2009) excepting the Richards-Baker Flashiness Index (FI_RB) (Baker et al., 2004), the flow permanence (MF) (Arscott et al., 2010) and the six-month seasonal predictability of dry periods (SD6) (Gallart et al., 2012).
The choice of index was driven by the ease of calculation and representativeness for temporary streams.
The 34 metrics computed using the IHA software package describe most of the major flow regime components and are deemed to be particularly relevant to aquatic communities (Olden and Poff, 2003). The datasets were normalised by watershed area to make the flow rates comparable because flow data came from watersheds of different sizes. IHA parameters were calculated using non-parametric statistics due to the skewed nature of the hydrological datasets.
FI_RB was introduced to the study because it represents a measure of flow variability and has an important place in the classification of Mediterranean streams. FI_RB is important in the classification of Mediterranean streams owing to the peculiarity of the region's precipitation events, which are highly variable in both time and space (Baker et al., 2004; Oueslati et al., 2015).

This index provides a useful characterisation of the way watersheds process hydrological inputs into their streamflow outputs.

The relative time with or without water flow is the metric used for identifying temporary streams and has a relevant ecological role because it allows the development of taxa adapted to living in temporary conditions (Arscott et al., 2010; Wissinger et al., 2008). For these reasons, the MF index (long-term annual mean relative number of months with flow) was selected. SD6 was also introduced to the study as a metric for characterising the seasonality of dry conditions (zero flow) of a stream reach. This index is easy to put into plain words in interviews when information from instruments is not available (Gallart et al., 2012).

HIs were computed using daily streamflow data considering the entire measured and simulated flow datasets.

3.1.3 Principal component analysis

Principal Component Analysis (PCA) was applied to identify the HIs that represent the main aspects of the flow regime and to identify patterns in gauging stations with similar hydrological characteristics (D'Ambrosio et al., 2017a). The purpose was to reduce the number of variables (HIs) and describe the same amount of variance with fewer variables. PCA was performed considering only measured stations' HIs.

PCA is a multivariate technique and is considered 'the mother of all methods in multivariate data analysis' (Varmuza and Filzmoser, 2008). PCA transforms data into a new orthogonal coordinate system whose axes or 'Principal Components (PCs) are defined by linear combinations of input data which are uncorrelated with each other. The greatest variance by any projection of the data comes to lie on the first PC, which explains the largest fraction of the original data variability. The second PC explains a smaller fraction of the data variance than the first and so forth.

The new orthogonal coordinate system was obtained by applying a Varimax rotation, which is the most widely employed orthogonal rotation in PCA. It is most common because it tends to produce simplification of the un-rotated loadings, allowing easier interpretation of the results (Abdul-Wahab et al., 2005; Sousa et al., 2007). It simplifies the loadings by rigidly rotating the PC axes such that the variable projections i.e. the loadings on each PC tend to be high or low.

Before applying PCA, the number of HIs was reduced on the basis of minimising statistical redundancy among metrics. This was achieved by checking the correlation matrix of indices and by considering the indices' significance for the study area features (Olden et al., 2012). Statistical analyses were performed using R-based software (gruppochemiometria.it).

PCA was carried out on the Spearman rank correlation matrix rather than the covariance matrix to ensure that all indices contributed equally and the contributions were scale-independent and less sensitive to higher values (Assani et al., 2006; Legendre and Legendre, 1998). Moreover, because HIs had different measurement units i.e. dimensionless or cubic meter per second per square kilometer (m^3 s^{-1} km^{-2}), input data were centred and scaled in both analyses so purpose that all columns had a zero mean (centring) and unit variance (scaling) (Wang and Xiao, 2004). In this way, each variable had the same 'weight' for PCA (Varmuza and Filzmoser, 2008).

Different methods exist to calculate the number of PCs (Fabrigar et al., 1999; Kaiser, 1960). In this study, the choice of the number of PCs to be retained was driven by the explained variance. Using this information, the chosen factors had to explain at least 75% of the variance. The HIs were considered to be significantly correlated with a PC when their loading value on one PC was at least 0.28.

3.1.4 MULTIPLE REGRESSION ANALYSIS

Selected indicators were linked to the catchment characteristics by fitting a multiple regression analysis (D'Ambrosio et al., 2017a). Catchment characteristics likely to affect the stream flow regimes and selected HI values, including measured and simulated streamflow (Table 1), were analysed as independent and dependent variables respectively.

Many studies have identified watershed size and shape, climate, geology, soil type, topography and land cover as features largely determining river flow regime patterns (Baker et al., 2004; Chiverton et al., 2015; Poff et al., 1997; Snelder and Biggs, 2002;). In this study, the criteria used to select the catchment characteristics were based on the availability of information and data for the study area. Indeed, the purpose of this analysis is to provide River Basin Authorities with a tool which can be used for estimating indicators characterising the hydrological regime and for classifying ungauged streams. Based on these assumptions and on data availability, the following characteristics were selected: catchment area (A), gauging station elevation (E), mean catchment elevation (Z), mean catchment slope (S), mean annual rainfall (MAR), land use (UDS), soil hydraulic conductivity (K) and available water content (AWC). Unfortunately, data concerning lithological and geological aspects were not available and consequently were not included, even if they may have a relevant influence on streamflow through such things as transmission losses or baseflow.

The source of each dataset and a brief description of the method used to derive the corresponding catchment features are provided in Table 3.

Table 3: Catchment characteristics derived from available data (D'Ambrosio et al., 2017a)

Catchment characteristics	Data source	Method
Catchment area A (km^2)	Digital Terrain Model (20 m resolution), National Carthographic Portal	ArcMap 10.2 Spatial Analyst Tools were used to derive the catchment area from the dataset
Gauging station elevation E (m)	Digital Terrain Model (20 m resolution), National Carthographic Portal	ArcMap 10.2 Spatial Analyst Tools were used to derive the measured and simulated station elevation
Mean catchment elevation Z (m)	Digital Terrain Model (20 m resolution), National Carthographic Portal	ArcMap 10.2 Spatial Analyst Tools were used to derive the mean elevation of catchments from the dataset
Mean catchment slope S (degrees)	Digital Terrain Model (20 m resolution), National Carthographic Portal	ArcMap 10.2 Spatial Analyst Tools were used to derive the mean catchment slope from the dataset
Mean annual rainfall MAR (mm)	Hydrological Annals, Part II, Section A (1965– 1996 for measured stations; 1990-2009 for simulated stations), Hydrographic service	Data reported into the Hydrological Annals were used without any elaboration
Artificial surfaces UDS1 (%)	1:100000 Corinne Land Cover 2000 (CLC class n. 1, 1st level) National Carthographic Portal	ArcMap 10.2 Analysis Tools were applied to the dataset to identify the extent of artificial surfaces within the catchments

Catchment characteristics	Data source	Method
Agricultural areas UDS2 (%)	1:100000 Corinne Land Cover 2000 (CLC class n. 1, 2nd level), National Carthographic Portal	ArcMap 10.2 Analysis Tools were applied to the dataset to identify the extent of agricultural areas within the catchments
Forest and semi natural areas UDS3(%)	1:100000 Corinne Land Cover 2000 (CLC class n. 1, 3rd level), National Carthographic Portal	ArcMap 10.2 Analysis Tools were applied to the dataset to identify the extent of forest and semi natural areas within the catchments
Catchment mean saturation hydraulic conductivity K (mm/hr)	1:100000 ACLA 2 Soil Maps, Puglia Region	ArcMap 10.2 Analysis Tools were applied to the dataset in order to achieve a soil type distribution within the catchments. The software Soil Water Characteristics 6.02.74, implemented by the USDA Agricultural Research Service, was used as mean saturation hydraulic conductivity calculator.
Soil available water content AWC (%)	1:100000 ACLA 2 Soil Maps, Puglia Region	ArcMap 10.2 Analysis Tools were applied to the dataset in order to achieve a soil type distribution within the catchments. The software Soil Water Characteristics 6.02.74, implemented by the USDA Agricultural Research Service, was used as soil available water content calculator.

Spearman rank correlation coefficients were used to check the degree of correlation between the catchment characteristics (Lo Presti et al., 2010). Therefore, the independent variables used in the study were those found to be uncorrelated. Regression analyses were then performed to assess the statistical significance of the relationship between the independent and dependent variables, and identify the best regression model. Two models were tested: linear and second-order polynomial. All the analyses were performed using R-software (r-project.org). Prior to modelling, where needed, the dependent and independent variables were transformed in order to meet the main assumptions underlying the regression models. Such assumptions concern the residuals coming from the modelling. However, in practice it is possible by means of an a priori transformation of the variables, to make the residuals inherit the desired properties. More specifically, the Gaussian normality and the homoscedasticity of the residuals can be achieved by subjecting the variables to skewed distributions via a Box-Cox transformation. In particular, the variables catchment area (A) and gauging station elevation (E) were subjected to such transformation. As the percentage variable (UDS) cannot vary freely because it ranges from 0-100% (or to 1.0) (Reinard, 2006), it was subjected to an arcsine-square root transformation for converting the percentages into scores that were less skewed than the original data. This process serves to equalise the local variance of data at the same time. Soil hydraulic conductivity (K) was logarithmically transformed whereas mean catchment slope (S) was expressed in radians.

The transformed variables were then checked for Gaussian characteristics with four different normality tests: Shapiro-Wilk, Anderson-Darling, Lilliefors and Jarque-Bera.

The adequacy of the two tested models was checked by means of an accuracy analysis. Many statistical indices are available but the Relative Mean Absolute Error (RMAE) provides many desirable properties. The RMAE measures the average departure of the predicted vs. the observed value using the observed value itself as the measurement unit. Therefore, it is easy to classify the predictive accuracy of the model using the RMAE value (Chai and Draxler, 2014; Willmott and Matsuura, 2005), calculated thus:

$$RMAE = \frac{1}{n}\sum_{i=1}^{n}\frac{|r_i|}{z_i} \qquad \text{eq.(1)}$$

where: ri is the i-th residual, obtained as predicted minus observed value, z_i is i-th observed value.

3.1.5 RIVER TYPE CLASSIFICATION

The hydrological regime, variability and predictability in flow, loss of flow continuity over time and space (availability of water) and habitats are the major characteristics used to identify 'non-perennial' streams (D'Ambrosio et al., 2017a). Arthington et al. (2014) distinguished temporary or intermittent streams from episodic or ephemeral streams as follows:

i. Temporary or intermittent. Streams where the seasonal loss of flow (usually from weeks to a few months) and continuity, results in high variability in the availability of water and habitat over time on a more or less predictable basis.
ii. Episodic or ephemeral. Streams that flow unpredictably, depending on precipitation events, and with hydrological continuity for only a short period of time (usually days to weeks).

Some EU member States in the WFD implementation process include a classification of non-perennial streams based on the flow duration. Since 2008 (D.M. 131/2008, 2008), Italy has used this stream type classification and defines rivers as:

i. Temporary. Rivers with dry periods all over the water body or only in parts of it, recorded either every year or at least twice within 5 years).
ii. Intermittent. Rivers that flow for more than 8 months per year.
iii. Ephemeral. Rivers that flow for less than 8 months per year but continuously.
iv. Episodic. Temporary rivers that are usually dry and flow only after intense rainfall events.

Spanish regulations (MARM/2656/2008, 10 Sep. 2008) classify non-perennial streams as temporary or seasonal (flow duration: 300-365 days per year), intermittent or strongly seasonal (flow duration: 100-300 days per year) and ephemeral (flow duration: <100 days per year).

As the presence of pools along the stream course is an important factor for biota, Gallart et al (2012) defined a river classification that takes into account the presence or absence of pools during the dry season. Plotting SD6 and MF indices, it is possible to identify four main conceptual types of streams as a function of aquatic meso-habitat occurrence. These four types are: perennial (P), intermittent-pools (I-P) (only subsurface flow occurs), intermittent-dry (I-D) (surface and subsurface flow are absent for at least one month a year) and episodic-ephemeral (E) (surface and subsurface flow is absent for at least 10 months a year) (Uys and O'Keeffe 1997). In this work this classification was adopted.

3.2 MEASUREMENTS IN SURFACE WATERS

Surface water in the Celone basin was sampled over a period of 12 months from June 2010 to July 2011 at a monitoring point (M. Pirro) coincident with the watershed's closing section (De Girolamo et al., 2017b). Unfortunately, due to the limited financial resources the monitoring activities were interrupted in July 2011.

An ISCO automatic sampler with internal data logger (mod. 6712FS; pumped volume 1 L; 24 bottles) was installed (Fig. 1). The sampler intake nozzle was positioned at the centre of the cross

section, vertically to the flow and was submerged as suggested by the US Geological Service manual (Edwards and Glysson, 1999).
The sampler was connected to a flow module (ISCO 750 Area-Velocity Flow Module) to determine channel flow. This sensor measured both the level of the flow and the velocity at which the water was moving. A predefined stage–discharge rating curve for flow conversion was choosen based on the cross section shape. Installation and programming of the device were done following the installation and operation guide (Teledyne ISCO, 2008).
A different frequency for water sampling in the diverse flow conditions was used. Periodic samples were taken at fortnightly or monthly time intervals during low flow, and once or twice a week during normal-flow conditions. During floods, with some exceptions, the time intervals varied from 15 min to 2 h over the rising limb of hydrograph and from 2 h to 1 day over the flood recession. The total number of samples from July 2010 to July 2011 was 210; the majority of the peak flow events were sampled for water quality except few events in November and February when the sampler pump tube was damaged.
The concentrations of ammonia ($N\text{-}NH_4$), nitrate ($N\text{-}NO_3$), nitrite ($N\text{-}NO_2$), and total nitrogen (TN) were determined in the IRSA-CNR laboratory using photometric method. The photometer (System MaxiDirect of ACQUA LYTIC) is mobile and offers the advantage to be a rapid and reliable water testing. Given the huge number of collected samples the analysis rapidity was a main feature of our selected method since it allowed the reduction of the time between the sampling and the analysis, therefore avoiding the risk of chemical modifications expected for non-conservative species. Total organic nitrogen (TON) was calculated as the difference between the TN and the sum of the inorganic nitrogen compounds ($DIN = N\text{-}NH_4 + N\text{-}NO_3 + N\text{-}NO_2$). The photometer was precalibrated appropriately before measurements and replicate analyses in laboratory using the APAT-IRSA/CNR analytical standard methods (Agenzia per la Protezione dell’Ambiente e per i servizi Tecnici – Istituto di Ricerca Sulle Acque/Consiglio Nazionale delle Ricerche, 2003).

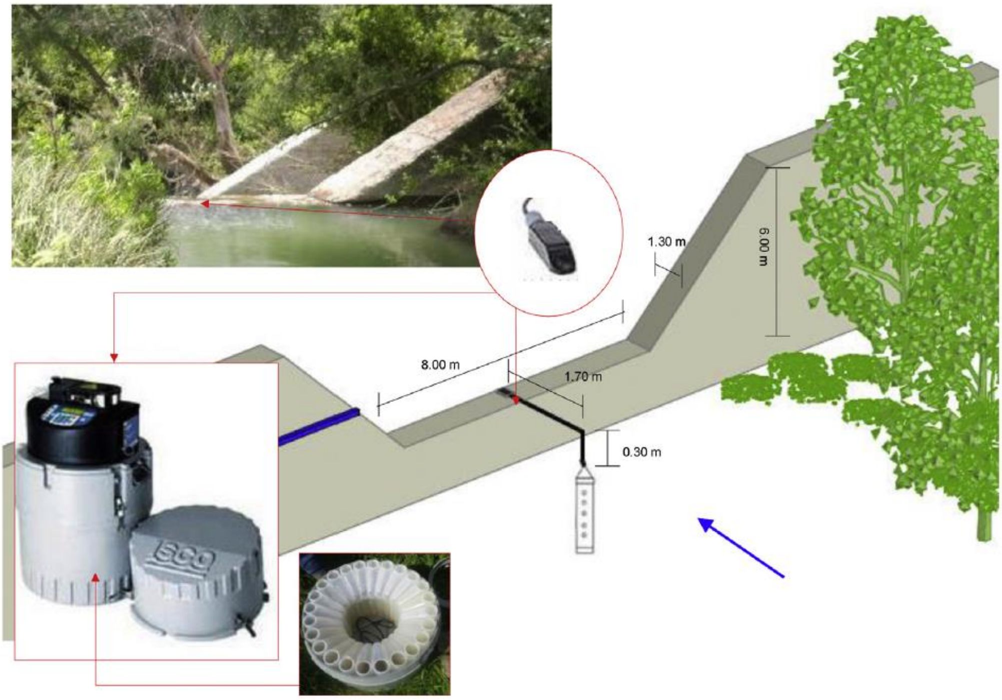

Fig. 1: Cross section of the Celone river, Masseria Pirro gauging station. Schematic view from upstream to downstream. The blue arrow indicates the flow direction (De Girolamo et al., 2017a)

Moreover, three sampling campaigns (September and November 2010, April 2011) were done to analyse nutrient concentrations upstream and down-stream from the discharge of the three waste water treatment plants (WWTPs), since no data was available. Thus, it was possible to estimate the input waste load associated to these three point sources (N_{PS}).

3.3 NITROGEN RIVERINE EXPORT ESTIMATION

It is well know that load passing through a river cross section during a time interval can be expressed by the following relationship (De Girolamo et al., 2017b):

$$L = \int_{t_1}^{t_2} Q_t C_t dt \qquad \text{eq.(2)}$$

where Q_t is the streamflow (l s^{-1}) at time t, C_t is the concentration (mg l^{-1}) at the time t (s), and L is the load (mg). This relation may be applied when Q_t and C_t measurements are simultaneous. Conversely, estimating loads when flow and concentration measurements are not continuous and simultaneous is not an easy task and several methodologies have been developed, that can produce significant discrepancies in the result (D'Ambrosio et al., 2017c; Letcher et al., 2002; Lewis et al., 2007; Moatar and Meybeck, 2005). In this study, monthly loads were determined using four different methods (i.e., inter-sample mean concentration; inter-sample mean concentration using mean flow; linear interpolation of concentration; concentration power curve fitting), which use some form of averaging in the calculation of the loads (Table 4). The Loads Tool (Marsh et al., 2006) was used, and four different values of monthly load were provided. Annual mean ($N_{RE,mean}$), minimum ($N_{RE,min}$) and maximum ($N_{RE,max}$) nitrogen riverine exports were then calculated.

Table 4: Load estimation methods

Method	Description	Load equation	
1	Inter sample mean concentration	$\sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} q_j$	c_j is the j^{th} sample concentration q_j is the j^{th} flow
2	Inter sample mean concentration (flow)	$\sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} \bar{q}_{<j+1}$	c_j is the j^{th} sample concentration $\bar{q}_{<j+1}$ is the average flow to the end of the j+1 period
3	Linear interpolation of concentration data	$\sum_{j=1}^{n} \frac{c_j + c_{j+1}}{2} q_j$	c_j is the j^{th} sample concentration q_j is inter-sample mean flow
4	Concentration power curve	$k \sum_{i=1}^{n} \frac{c_i}{n} \sum_{i=1}^{n} \frac{q_i}{n} = k\bar{c}\bar{q}$	c_i is the i^{th} concentration when it exists and aq_i^b otherwise a is a calculated coefficient q_i is the i^{th} sampled discharge (flow) b is the calculated power $\bar{c}$ is average of n concentration measurements $\bar{q}$ is average of n discharge measurements k is number of time intervals in period (eg. k=365)

Before using the Loads Tool, daily equivalent TN concentrations were evaluated from the measurements for those days during which several samplings were done (i.e., flood events) (De Girolamo et al., 2017a; De Girolamo et al., 2017b; De Girolamo et al., 2015c; De Girolamo et al., 2012).

As the streamflow data ($m^3\ s^{-1}$) were measured on 15 min time interval, linear interpolated concentrations were calculated between two consecutive observations when the time interval of sampling was longer than 15 min to have streamflow and concentrations values on the same time interval. Then, the following equation to calculate daily load was used:

$$DailyL = 0.9 \sum_{t=1}^{96} q_i C_{\text{int}} \qquad \text{eq.(3)}$$

where DailyL is the daily load (kg) passing through the river section; q_i is the measured streamflow (l) at time interval t (1, 2, …96); C_{int} is the measured or linearly interpolated concentration (mg l^{-1}) at the time t (1, 2, …96), 0.9 is the time interval (15·9·60 = 900 s which includes the conversion factor 1000^{-1}). The daily equivalent concentration of each chemical compound during the floods was obtained by dividing the DailyL by the daily volume.

3.4 ANALYSIS OF LOCAL AGRICULTURAL PRACTICES

The necessary agronomic data were provided by interviews with farmers and local dealers, which were selected precisely in order to gain information covering the whole Celone catchment (D'Ambrosio et al., 2017b; D'Ambrosio et al., 2017c).

The collected information includes type, timing and amount of fertilisers used for each crop, annual crop yields, crop rotation, tillage operations and irrigation supply.
The amount of the TN application rate was estimated for each crop within the catchment boundaries, including TN in synthetic fertilisers (N_{SF}) and animal manure (N_{AF}). 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 (D.M. 7 aprile 2006, 2006; Perelli and Pimpini, 2003). A distinction between indoor and outdoor farming was made. For manure produced by indoor farming, 27.5% of TN loss during manure handling and storage was considered (Fulhage and Pfost, 2002).
Crossing data from the National Agricultural Census (ISTAT, 2010) with data from local surveys and field inspections, the land use initially defined from a regional map (Corine Land Cover – IV Level, http://www.pcn.minambiente.it) was reclassified, and a detailed land cover map was obtained (Fig. 6).

3.5 NITROGEN BALANCE ASSESSMENT

The soil N balance was performed for the period July 2010 - June 2011. Anthropogenic pressures in the Celone watershed were then analysed and non-point sources of N were quantified The fluxes of N entering and leaving the Celone river basin were accurately estimated in the study period (De Girolamo et al., 2017a). The N input and output across the area were included in the following equation to estimate the soil system budget:

$$(N_{SF} + N_{AF} + N_{BF} + N_{AD}) - (N_{CU} + N_{V} + N_{D}) = \Delta N \qquad \text{eq.(4)}$$

where: N_{SF} is N from fertilizers; N_{AF} is N input from animal farming; N_{BF} is biological fixation; N_{AD} is N input from atmospheric depositions; N_{CU} is N-uptake; N_{V} is ammonia (NH_3) volatilization from urea and ammonium nitrate; and N_{D} is denitrification in soils.

3.5.1 NITROGEN INPUT

In the Celone catchment, anthropogenic N inputs include diffuse sources, such as chemical fertilizers and animal manure.

3.5.1.1 Nitrogen from fertilizer application

As above mentioned, data from Agricultural Census (ISTAT, 2010) and local Authorities were collected and integrated with information from farmers and local dealers’ interviews (De Girolamo et al., 2017b).
Official statistics provided by the Italian National Institute of Statistics (ISTAT, 2010) concerning fertilizers were not used because these data are available only at provincial level. The Celone catchment lays within the province of Foggia which includes also an intensive agricultural area (i.e. Tavoliere Plain) outside the investigated catchment, thus the downscaling of provincial data could overestimate the average fertilizer application for the study area (De Girolamo et al., 2017a). Taking into account that agronomic techniques adopted in the upper basin are different from those commonly used in the lower part of the basin, the farmers were accurately selected in order to have information covering the whole study area.

On this basis, N in chemical fertilizers was evaluated for each crop in the watershed boundaries and finally the total amount of N from fertilizers (N_{SF}).

3.5.1.2 Nitrogen from animal farming

In order to evaluate N input from animal farming (N_{AF}) and the supply of manure to agricultural lands, livestock densities were collected by crossing data from the National Agricultural Census (ISTAT, 2010) with data from local surveys provided by a vet operating in the area (De Girolamo et al., 2017a; De Girolamo et al., 2017b). N input from livestock manure was calculated by multiplying the live weight of each animal type by the animal-specific N excretion rates (Bonciarelli, 1989; D.M. 7 aprile 2006, 2006; Perelli and Pimpini, 2003). A distinction between indoor and outdoor farming was made. For manure produced by indoor farming, 27.5 % of TN losses during manure handling and storage was considered (Fulhage and Pfost, 2002).

3.5.1.3 Nitrogen from atmospheric deposition

N input from atmospheric depositions (N_{AD}) was estimated on the basis of recorded data in a gauging station of the CONEFOR network (LIFE+ Futmon Project) located in Puglia Region: Foresta Umbra (PUG1) (Marchetto et al., 2014). This station is characterized by the same characteristics in terms of climate and land use of the Celone catchment.

3.5.1.4 Nitrogen from biological fixation

N input from biological fixation (N_{BF}) was estimated by multiplying the total rate and the surface of each N-fixing crop type (mainly broad beans, vetch and legumes) cultivated within the basin (De Girolamo et al., 2017a). Total N fixation rates were calculated as the sum of two contributions, i.e. the N fixed in the harvested aboveground tissues (annual yield multiply by N content) plus the N fixed in the not harvested belowground biomass that remains in the soil at the end of a cultivation cycle (Castaldelli et al., 2013). The latter amount, not considered as an output in the balance, was estimated as 52.5 kg N ha^{-1} yr^{-1}, 42.5 kg N ha^{-1} yr^{-1}, 10 kg N ha^{-1} yr^{-1} for field bean, vetch, and legume crops, respectively. Finally, literature N fixation rates of 15 kg N ha^{-1} yr^{-1} for pasture with legumes (Bassanino et al., 2007), and 10 kg N ha^{-1} yr^{-1} for deciduous forest, olive trees and orchards (Burns and Hardy, 1975; Jordan and Weller, 1996) were adopted.

3.5.2 NITROGEN OUTPUTS

Major N output includes crop N-uptake (N_{CU}), ammonia (NH_3) volatilization from urea and ammonium nitrate (N_V) and denitrification (N_D) (De Girolamo et al., 2017a). 10% of N from urea and ammonium nitrate were assumed to be lost by NH_3 volatilization (N_V) (Isidoro et al., 2006), while N removed with harvest was estimated for the main cultivations by multiplying specific yield and crop uptake coefficient (Grignani et al., 2003; Regione Emilia-Romagna, 2007; Regione Lombardia, 2007).

Crop yields were obtained by local farmers' interviews. N_D were assumed as 10% of supplied N to agricultural lands, while the denitrification from non-productive land was consider negligible (Smil, 1999).

3.5.3 NITROGEN INPUT FROM POINT SOURCES

In the Celone catchment, anthropogenic N inputs include point sources, which are treated wastewaters coming from three treatment plants (2863 Equivalent Inhabitants, EI) that are discharged into the river (De Girolamo et al., 2017a).
Only monthly waste volumes discharged into the river were provided by the on-site operator and two values of TN concentrations for each plant, recorded in December and March, upstream and downstream from the inlet. As mentioned in the paragraph 3.2, three sampling campaigns (April, September 2010 and November 2011) were done to detect nutrient concentrations upstream and downstream from the inlet in order to have additional data.
The following equation to estimate the input waste load (Q_wC_w) was used:

$$Q_rC_r - Q_uC_u = Q_wC_w \qquad \text{eq.(5)}$$

where: Q_u is the upstream flow ($m^3\ s^{-1}$); Q_w is the waste water flow rate; Q_r is the flow rate downstream the source; C_u is the upstream total N concentration ($mg\ l^{-1}$); C_w is the concentration in the waste water; C_r is the concentration downstream. The flows and concentrations were assumed to be the same along the month as in the day of sampling.

3.6 ASSESSMENT OF THE WATER FOOTPRINT

In this study, the WF assessment was performed following the calculation framework proposed by Hoekstra et al. (2011), and depicted in Fig. 2 (D'Ambrosio et al., 2017c). 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, as reported in the following equation:

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

The WFs associated with single crops, and then with the entire watershed, were evaluated. A time interval of 10 days was considered for all the WF estimates, to provide a better representation of hydrological processes, and understanding of water use and scarcity (Savenije, 2000). Moreover, the watershed was divided into 'land use systems' (LUSs), defined as areas with similar land use, soil characteristics and precipitation amounts (Savvidou et al., 2016; Smaling et al., 1993). In particular, four rainfall zones (Thiessen polygons), two hydrological soil groups (C, D) (USDA - Soil Conservation Service, 1985) and 24 land-use classes have been distinguished and, hence, 103 LUSs have been identified (D'Ambrosio et al., 2017b).

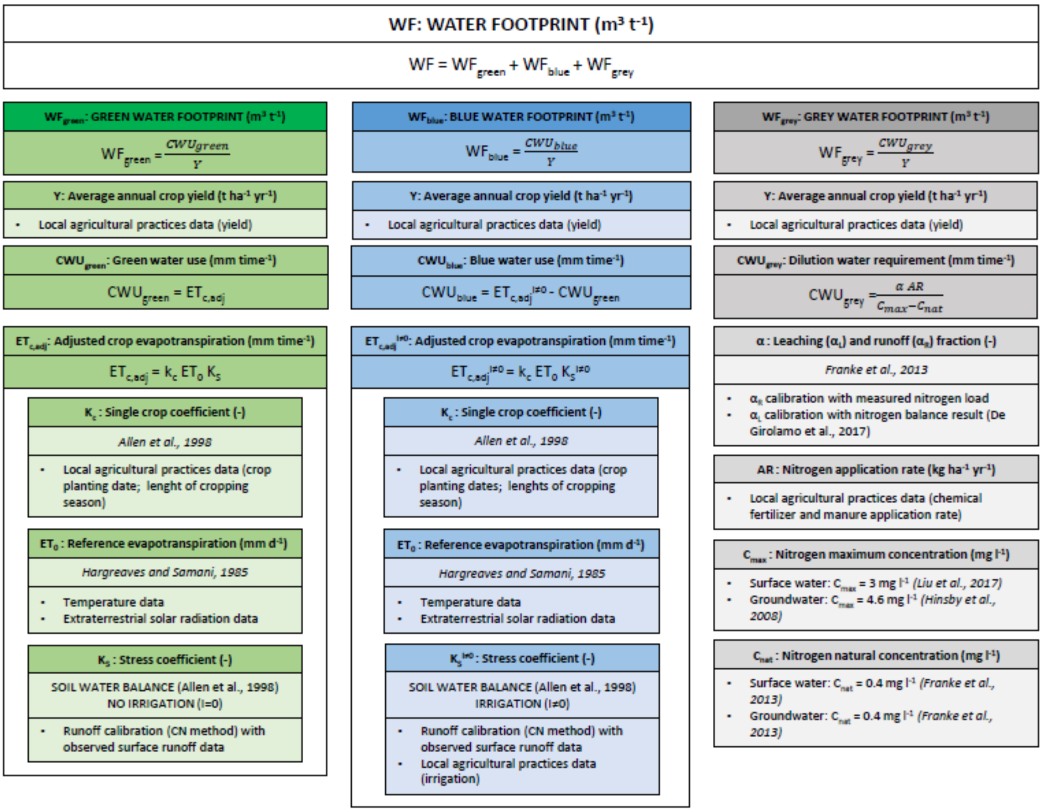

Fig. 2: WF assessment methodological scheme (D'Ambrosio et al., 2017b)

3.6.1 GREEN WATER FOOTPRINT

The WF_{green} is calculated as the ratio of the volume of green water used (CWU_{green}) for crop production (m^3 ha^{-1} yr^{-1}), to the average annual crop yield (Y) produced (t ha^{-1} yr^{-1}) (Hoekstra et al., 2011):

$$WF_{green} = \frac{CWU_{green}}{Y} \qquad \text{eq.(7)}$$

CWU_{green} refers to the part of precipitation that is temporarily stored in the soil and/or on top of the soil or vegetation and, hence, does not runoff or leach (D'Ambrosio et al., 2017c). This water can evaporate or transpire through plants and be an important factor in agricultural production, especially for rain-fed croplands (Falkenmark et al., 2003).

A multitude of different empirical formulae or crop models exist to estimate CWU_{green} in agriculture (Hoekstra et al., 2011). In this study, the 'irrigation schedule option' procedure was used, since it better simulates the water stress conditions that are typical of Mediterranean regions (Blinda et al., 2007). 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 ($ET_{c,adj}$):

$$CWU_{green} = ET_{c,adj} = K_c\, ET_0\, K_s \qquad \text{eq.(8)}$$

, 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).
The computations of $ET_{c,adj}$ have been done following methods and assumptions provided by Allen et al. (1998).
Since K_c varies in time as a function of the plant growth stage, 10-day average single crop coefficients ($K_{c,i}$) were calculated for each crop in the study area from the crop coefficient curves, which were constructed using initial K_c ($K_{c,ini}$), middle K_c ($K_{c,mid}$) and end K_c ($K_{c,end}$), as reported by Allen et al. (1998), Lazzara and Rana (2010) and Vanino et al. (2015). Crop planting dates and lengths of cropping seasons were provided from the above-mentioned interviews with farmers and local dealers. Table 5 summarises for each crop the various coefficient used in the equations (8) in order to obtain $K_{c,i}$.

Referring to the calculation methodology adopted for the ET_0 estimate (mm d^{-1}), the following equation (Hargreaves and Samani, 1985) was applied to 12 temperature gauges (D’Ambrosio et al., 2017c):

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

, where λ is the latent heat of vaporisation (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. Temperature gauges were chosen within a 25 km buffer around the Celone watershed, considering temperature data availability (January 2010 – June 2011).
The Hargreaves and Samani (1985) equation was used because solar radiation, relative humidity and wind speed data, required by other methods (Allen et al., 1998; Lingling et al., 2013), are missing in the Celone watershed.
Daily temperature data were sourced from the ‘Hydrological Annals’ of the Puglia (www.protezionecivile.puglia.it) and Campania (http://centrofunzionale.regione.campania.it/) Regions. Daily λ was obtained by applying the Harrison (1963) formula, as follows:

$$\lambda = 2.5 - 0.002 * T_{mean} \qquad \text{eq.(10)}$$

The values assumed by daily RA from the 12 temperature gauges were provided by the National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA).
Daily ET_0 was calculated by applying the equation (9), which was then appropriately summed in order to obtain values on a 10-day basis ($ET_{0,i}$) (D’Ambrosio et al., 2017c).

Finally, a GIS-based Inverse Distance Weighted method was used, in order to spatially interpolate the 12 punctual $ET_{0,i}$ values in the entire watershed, considering a time-interval of 10 days (Güler et al., 2014; Tao et al., 2015).

Table 5: Crop coefficient, length of crop development stages, plant date, depletion fraction (p) and maximum effective rooting depth (Zr)

Crop	Crop coefficient			Length of crop development stages (day)					Plant date	p	Z_r (m)*
	$K_{c,ini}$	$K_{c,mid}$	$K_{c,end}$	L_{ini}	L_{dev}	L_{mid}	L_{late}	Total			
Durum wheat	0.30	1.15	0.25	40	60	60	40	200	Nov	0.55	1.3
Deciduous forest	0.52	0.92	0.68	20	70	120	60	270	Mar	0.47	1.5
Olive grove	0.65	0.70	0.70	30	90	60	90	270	Mar	0.65	1.5
Vetch	0.50	1.15	1.10	20	30	35	15	100	Mar	0.45	0.6
Sunflower	0.35	1.08	0.35	25	35	45	25	130	Apr	0.45	1.2
Pasture	0.40	0.85	0.85	20	30	35	15	100	Mar	0.60	1
Winter wheat	0.70	1.15	0.25	30	140	40	30	240	Nov	0.55	1.7
Field bean	0.50	1.15	1.10	20	30	35	15	100	Mar	0.45	0.6
Bushes and shrubs	0.52	0.92	0.68	20	70	120	60	270	Mar	0.47	1.5
Urbanized area	0.00	0.00	0.00	-	-	-	-	365	-	-	-
Set-aside land	0.20	0.20	0.20	-	-	-	-	365	-	-	-
Deciduous and coniferous forest	0.35	0.68	0.65	20	70	120	60	270	Mar	0.47	1.5
Herbage (multiannual)	0.50	1.15	1.10	20	30	35	15	100	Mar	0.45	0.6
Herbage	0.70	1.20	0.60	20	25	25	10	80	May	0.55	1.4
Legumes	0.50	1.15	1.10	20	30	35	15	100	Mar	0.35	0.8
Orchard	0.52	0.92	0.68	20	70	120	60	270	Mar	0.47	1.5
Coniferous forest	1.00	1.00	1.00	-	-	-	-	365	-	0.70	1.5
Vegetable crop	0.50	0.95	0.75	25	35	25	15	100	Apr	0.50	0.8
Tomato	0.95	1.25	0.85	30	40	45	30	145	Apr	0.40	1.1
Vineyard	0.30	0.70	0.45	30	60	40	80	210	Apr	0.45	1.5
Sugar beet	0.35	1.20	0.70	45	75	80	30	230	Nov	0.55	1
Crucifers	0.70	1.05	0.95	30	35	90	40	195	Sep	0.45	0.6
Potato	0.50	1.15	0.75	25	30	30	30	115	Feb	0.35	0.5
Orchard and vegetable crop	0.80	1.18	0.85	20	70	120	60	270	Mar	0.35	1.5

* Zr used in equation (12) was the lowest value between the depth of the soil and that tabulated here

After calculating the crop evapotranspiration under standard conditions ($ET_{c,i} = K_{c,i}\ ET_{0,i}$), K_s was evaluated as follows (following Allen et al., 1998):

$$\begin{cases} K_{s,i} = \dfrac{TAW - D_{r,i-1}}{TAW - RAW} & D_{r,i-1} > RAW \\ K_{s,i} = 1 & D_{r,i-1} \leq RAW \end{cases} \qquad \text{eq.(11)}$$

, 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-day period considered. Formulae (12) and (13) were used to assess TAW and RAW values, respectively:

$$TAW = 1000(\theta_{FC} - \theta_{WP})Z_r \qquad \text{eq.(12)}$$

$$RAW = p\,TAW \qquad \text{eq.(13)}$$

, 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. (1998).
The θ_{FC} and θ_{WP} depend on the type of soil, and average values were estimated with the software Soil Water Characteristics, implemented by the USDA Agricultural Research Service. Z_r was 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. (1998) (Table 5).

Lastly, a water balance computation for the root zone was implemented on a 10-day basis, in order to estimate the root zone depletion at the end of the 10-day period ($D_{r,i}$) (mm) (D'Ambrosio et al., 2017c). Hence, a GIS model with 20-m resolution was developed. According to Allen et al. (1998), the incoming (irrigation, rainfall) and outgoing (runoff, deep percolation, evapotranspiration) water flux into the crop root zone were assessed (Fig. 3). Water transferred horizontally by subsurface flow in or out of the root zone was ignored. Moreover, being that the groundwater table is more than about 1 m below the bottom of the root zone, also the amount of water transported upwards by capillary rise was assumed to be zero.

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

$$D_{r,i} = D_{r,i-1} - P_{n,i} + RO_i - I_i + ET_{c,adj,i} + DP_i \qquad \text{eq.(14)}$$

, 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.

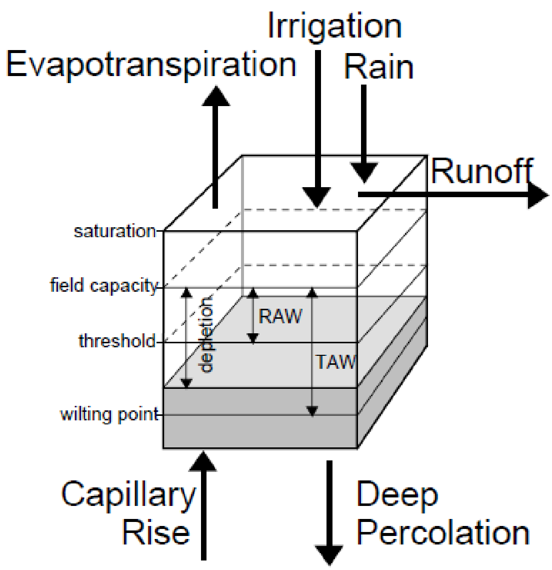

Fig. 3: Water balance of the root zone. The figure is extrapolated from Allen et al. (1998)

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

$$P_{n.i} = P_i - 0.2ET_{0,i} \qquad \text{eq.(15)}$$

, where P_i (mm) is the total precipitation amount. Precipitation gauges were chosen within a 25 km buffer around the Celone watershed, considering data availability (January 2010 – June 2011) (D'Ambrosio et al., 2017b). Thiessen polygons were built, and four rainfall zones were distinguished (Savvidou et al., 2016; Smaling et al., 1993). $ET_{c,adj,i}$ was determined according to equations (8) and (11), meanwhile equation (16) was used for DP_i determination:

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

The I_i values were set to be zero also for irrigated crops, both in equations (14) and (16), in order to estimate CWU_{green} (Hoekstra et al., 2011; Mekonnen and Hoekstra, 2011).
RO_i was estimated using the Soil Conservation Service Curve Number (SCS-CN) method (USDA - Soil Conservation Service, 1985), which is one of the most commonly-used models, due to its simplicity and requirement for few data (D'Ambrosio et al., 2017c; Ponce and Hawkins, 1996; Xiao et al., 2011). This model is used to predict the depth of surface runoff (RO) (in mm) for a given rainfall event, and can be expressed as follows:

$$\begin{cases} RO = \dfrac{(P - 0.2S)^2}{P + 0.8S} & P > 0.2S \\ RO = 0 & P \leq 0.2S \end{cases} \qquad \text{eq.(17)}$$

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

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

, where CN is the curve number (dimensionless) that ranges from 1 (minimum runoff) to 100 (maximum runoff). This parameter has been determined and tabulated based on hydrological soil group and soil cover type, treatment and hydrological condition (USDA, 1986). The tabulated values (CN II) refer to the average antecedent moisture condition (AMC II). The antecedent moisture condition (AMC) definition depends on the total five-day antecedent rainfall, and the season category (dormant or growing) that is defined from daily average temperatures (De Paola et al., 2013). Different CN-conversion formulae from AMC II, to dry AMC (AMC I – CN I) and wet AMC (AMC III – CN III), have been proposed (Mishra et al., 2008). In this study, the Hawkins et al. (1985) CN-conversion formulae were used (D'Ambrosio et al., 2017c).

Summing up, CN II tabulated values were associated with each LUS identified in the basin; AMC was evaluated for the four rainfall zones and, if necessary, CN I and CN III were calculated. Afterwards, equations (17) and (18) were applied, and the runoff associated with single precipitation events was estimated for each LUS. Considering a 10-day time interval, the runoff was appropriately added, and preliminary RO_i (mm) were obtained. These latter values were then modified, following the calibration procedure described below, and based on the continuous flow measurements at the gauge.

Daily mean baseflow (BF) (m^3 s^{-1}), daily mean interflow (IF) (m^3 s^{-1}) and total daily mean waste water discharge (WW) (m^3 s^{-1}) were subtracted from the mean daily streamflow recorded at MP (Q_{MP}) (m^3 s^{-1}), as follows:

$$SF_{MP} = Q_{MP} - BF - IF - WW \qquad \text{eq.(19)}$$

, where SF_{MP} (m^3 s^{-1}) is the estimated daily mean stormflow. Q_{MP} was obtained from the continuous measures of flow; BF and IF were assessed by means of the Baseflow Filter Program (swat.tamu.edu/software/baseflow-filter-program), whilst the WW value was provided by the Puglia Region, and is equal to 0.025 m^3 s^{-1}. Appropriately converting the units of measurements, and considering the 10-day time periods (i), volumes of surface runoff ($SF_{MP,i}$) (m^3) were estimated through the study period.

Therefore, CN values associated with each LUS were recalculated, so that the sum of RO_i ($\sum RO_i$) (m^3), calculated with equation (12), were equal to $SF_{MP,i}$ (m^3) (the target function). To do this, a spreadsheet was specifically created, and the target function was set (D'Ambrosio et al., 2017c).

Finally, calibrated CN values were used to estimate the RO_i (mm), required for the soil-water balance.

The water balance for the root zone (equation (9)) was initiated in the first 10-day period of January 2010 (Jan10 I), which was a really wet period. Therefore, it was assumed that, on Jan10 I, the root zone was near field capacity and, hence, $D_{r,Jan10\ I-1} = 0$, $K_{s,Jan10\ I} = 1$, and $ET_{c,adj,Jan10\ I} = ET_{c,Jan10\ I}$ (Zhuo et al., 2016)

3.6.2 BLUE WATER FOOTPRINT

The WF_{blue} refers to the consumption of ground and/or surface water resources that are utilised in crop production (i.e., irrigation water) (Hoekstra et al., 2011). 'Consumption' refers to the loss of water, which occurs when evapotranspired water returns to another catchment, or to the sea, or is incorporated into products (D'Ambrosio et al., 2017c). In other words, it is the amount of ground and/or surface water that does not return to the source in the form of return flow, and it is different from water withdrawn for irrigation, insofar as this water is returned to where it came from.

The WF_{blue} was calculated by dividing the total volume of blue water use, CWU_{blue} ($m^3\ ha^{-1}\ yr^{-1}$), by the quantity of the annual production, Y ($t\ ha^{-1}\ yr^{-1}$):

$$WF_{blue} = \frac{CWU_{blue}}{Y} \quad \text{eq.(20)}$$

The CWU_{blue} ($mm\ time^{-1}$) was calculated by performing another soil-water balance (equation (14)) on a 10-day basis, and irrigation (I_i) was considered, as proposed by Hoekstra et al. (2011) and applied by Mekonnen and Hoekstra (2011), de Miguel et al. (2015) and Zhuo et al. (2016). I_i values were deduced from the interviews mentioned in Section 3.4. The following equation was then used:

$$CWU_{blue} = ET_{c,adj}^{I\neq 0} - ET_{c,adj} \quad \text{eq.(21)}$$

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

3.6.3 GREY WATER FOOTPRINT

The WF_{grey} is referred to the volume of water needed to dilute a load of pollutants discharged into the natural water system in such a way that the quality of the receiving water body remains constant, with respect to specific quality standards and natural background concentrations (Franke et al., 2013; Liu et al., 2017). In this study, we quantified the WF_{grey} related to nitrogen use, thus excluding the effect 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 (D'Ambrosio et al., 2017c).

The WF_{grey} (m^3 t^{-1}) was quantified by dividing the dilution water requirement, CWU_{grey} (m^3 ha^{-1} yr^{-1}), by the crop yield, Y (t ha^{-1} yr^{-1}) (Hoekstra et al., 2011):

$$WF_{grey} = \frac{\mathrm{CWU}_{grey}}{Y} \qquad \text{eq.(22)}$$

The CWU_{grey} (mm yr^{-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} yr^{-1}), and dividing this by the difference between the maximum (C_{max}) and natural (C_{nat}) concentration (mg l^{-1}) of TN in the water bodies:

$$CWU_{grey} = \frac{\alpha * AR}{C_{max} - C_{nat}} \qquad \text{eq.(23)}$$

The AR was estimated for each LUS, based on the above-mentioned interviews. TN inputs due to chemical fertilisers and manure were then quantified.

In most of the previous studies, α is set at a constant value of 10% (Chapagain et al., 2006; Mekonnen and Hoekstra, 2011; Zhuo et al., 2016), or 7% (Stathatou et al., 2012). In contrast to the use of a static α throughout the watershed, the procedure suggested by Franke et al. (2013), and applied by Brueck and Lammel (2016), Munro et al. (2016) and Gil et al. (2017), was preliminarily used in this study (D'Ambrosio et al., 2017c). This approach considers that α depends on potential factors, (j), that 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:

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

, 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. (2013) provided specific criteria used to score (s) and weight (w) all the different influencing factors (j) that were applied in this study (D'Ambrosio et al., 2017b), considering the entire study period (July 2010 – June 2011). According to these specific criteria, all LUSs are located in areas of low TN deposition, have a clay (soil D) or loam (soil C) texture, are poorly- to very poorly-drained (soil D) or moderately to imperfectly drained (soil C), and subjected to average management practices. Notably, annual precipitation of 600–1200 mm ranked all LUSs into the group 'low'. Lastly, information concerning TN deposition, fixation and plant uptake was taken from the 'Soil System Budget' method, focussing on the Celone watershed (De Girolamo et al., 2017a).

Unlike previous studies, α_k was divided between leaching ($\alpha_{L,k}$) and runoff ($\alpha_{R,k}$) (D'Ambrosio et al., 2017c). Then, a zero weight ($w_{j,k}$) was assigned to factors specifically related to runoff (i.e., texture and natural drainage relevant for runoff) and leaching (i.e., texture and natural drainage relevant for leaching), respectively. Afterwards, $\alpha_{L,k}$ and $\alpha_{R,k}$ were recalculated, following a calibration procedure based on the field measurements (McFarland and Hauck, 2001). The applied procedure relies on equations (25) and (26):

$$R = \sum_{k=1}^{103} \alpha_{R,k}\ AR_k\ A_k \qquad \text{eq.(25)}$$

$$L = \sum_{k=1}^{103} \alpha_{L,k}\ AR_k\ A_k \qquad \text{eq.(26)}$$

, where $\alpha_{R,k}$ and $\alpha_{L,k}$ are the runoff and leaching fraction associated with the LUS k, AR_k (kg ha^{-1} yr^{-1}) is the application rate associated with the LUS k, A_k (ha) is the surface of the LUS k, R (kg yr^{-1}) is the TN runoff, estimated at the watershed closing section, whilst L (kg yr^{-1}) is the TN in soil and leaching. These last two parameters have to be equal to the following terms:

$$R = N_{RE} - N_{BF} - N_{AD} - N_{PS} - N_{NAT} \qquad \text{eq.(27)}$$

$$L = D - (N_{RE} - N_{PS} - N_{NAT}) - N_{BF,\ soil\,D} - N_{AD,\ soil\,D} \qquad \text{eq.(28)}$$

, where N_{RE} (kg yr^{-1}) is the TN riverine export, N_{BF} (kg yr^{-1}) is the TN biological fixation, N_{AD} (kg yr^{-1}) is the TN atmospheric deposition, N_{PS} (kg yr^{-1}) is the TN in wastewater sludge, N_{NAT} (kg yr^{-1}) is the TN naturally present in the river, D (kg yr-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 D (5,600 ha), where infiltration does not occur. The values of L were set to be greater than zero. N_{BF} (64,891 kg yr^{-1}), N_{AD} (39,744 kg yr^{-1}) and D (306,397 kg yr^{-1}) were taken from De Girolamo et al. (2017a). N_{NAT} was assessed by appropriately multiplying C_{nat} for the total discharge, Q_{TOT} (m^3 yr^{-1}), measured at MP. N_{RE} ($N_{RE,mean}$; $N_{RE,max}$; $N_{RE,min}$) and N_{PS} were determined, as described in Section 3.3.

The values of $\alpha_{R,k}$ and $\alpha_{L,k}$ were calibrated, in order to meet the results of equations (25) and (26), each of which generate three equations, considering $N_{RE,mean}$, $N_{RE,max}$ and $N_{RE,min}$ (D'Ambrosio et al., 2017c). Thus, the values of $\alpha_{R,k}$ and $\alpha_{L,k}$, initially obtained with equation (24), were multiplied by three different constant factors, respectively. A spreadsheet was specifically created, and a target function was set.

Regarding the C_{max} value in equation (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 (1974), and was continued by Postel et al. (1996) and Chapagain et al. (2006), 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 (Liu et al., 2017). Generally, WF_{grey} assessments 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 $N\text{-}NO_3$ l^{-1}) or the European Union/World Health Organization (50 mg NO_3 l^{-1}, i.e., 11.3 mg $N\text{-}NO_3$ l^{-1}) nitrogen standards for drinking-water are the most commonly used water-quality standards (Cazcarro et al., 2016; Chapagain et al., 2006; Chapagain and Orr, 2009; Mekonnen and Hoekstra, 2011, 2010; Stathatou et al., 2012). 50 mg NO_3 l^{-1} is also the maximum concentration permitted by the EU Nitrate Directive in groundwater. In the literature, only a few studies have used ambient water-quality standards (Pellegrini et al., 2016; Pellicer-Martínez and Martínez-Paz, 2016a; Zhuo et al., 2016). In Italy, the Decree of the Ministry of the Environment n. 260/2010 (D.M. 260/2010, 2010) identifies, among various physico-chemical factors, the threshold concentrations of NH_4, NO_3 and NO_2 that are required to support a functioning ecosystem. Concerning the 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 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. (2017), the TN ambient water-quality standard (good), adopted in this study for surface water, is 3 mg TN l^{-1}. Meanwhile, the standard adopted for groundwater is 4.6 mg TN l^{-1} (Hinsby et al., 2008).

Regarding the C_{nat} value in equation (18), many previous studies considered this value equal to zero, due to a lack of data (e.g., Chapagain et al., 2006; Mekonnen and Hoekstra, 2010; Stathatou et al., 2012; Zeng et al., 2013; Pellegrini et al., 2016); however, such an assumption leads to an underestimation of CWU_{grey} because C_{nat} is generally higher than zero. In this study, since local data are not available, the C_{nat} of TN was set to be 0.4 mg N l^{-1} in both river water and groundwater, as recommended by Franke et al. (2013), and used by Mekonnen and Hoekstra (2015) and Liu et al. (2017).

Finally, CWU_{grey} was estimated by summing the values associated with runoff ($CWU_{grey,r}$) and leaching ($CWU_{grey,l}$). For comparison, the most commonly-used values for α (10%), C_{max} (10 mg l^{-1}) and C_{nat} (0 mg l^{-1}) were also used for the CWU_{grey} (CWU_{grey}^C) and WF_{grey} (WF_{grey}^C) calculations. Finally, the uncertainty in the WF_{grey} estimate, related to α, C_{max} and C_{nat} variability, was assessed (D'Ambrosio et al., 2017b).

3.7 WATER FOOTPRINT SUSTAINABILITY ASSESSMENT

In order to assess whether the WFs are sustainable, the WF_{green}, WF_{blue} and WF_{grey} were compared with their maximum values associated with the Celone River basin to maintain sustainability (D'Ambrosio et al., 2017b). Hence, green water scarcity (WS_{green}), blue water scarcity (WS_{blue}) and water pollution level (WPL) were calculated. The evaluation was performed according to Hoekstra et al. (2011), and is described below.

3.7.1 GREEN WATER SCARCITY

The environmental sustainability of the WF_{green} was evaluated by means of the WS_{green}, which is defined as the ratio of the total of $\sum WF_{green}$ in the catchment to the green water availability, WA_{green}, within a certain period:

$$WS_{green} = \frac{\sum WF_{green}}{WA_{green}} \qquad \text{eq.(29)}$$

Being a ratio, the WS_{green} indicates the degree of green water use in a catchment. A WS_{green} equal to 1 means that the available green water has been fully consumed (Hoekstra et al., 2011). If higher than 1, the use throughout the watershed is unsustainable, whereas if lower than 1, the use is suitable, and green water is enough to meet the crops' demands without being harmful to natural areas.
The WA_{green} (m^3 $month^{-1}$) was calculated by this equation:

$$WA_{green} = ET_{green} - ET_{env} - ET_{unprod} \qquad \text{eq.(30)}$$

, where ET_{green} is the volume of green water, ET_{env} is the environmental green water requirement, and refers to the quantity of green water used by natural vegetation, that is important to preserve biodiversity and natural ecosystems within the catchment. Meanwhile, ET_{unprod} is the evapotranspiration from land that cannot be made productive in crop production.
According to Schyns et al. (2015), the cause of a non-widespread use of the WS_{green} index must be sought in the determination of these two parameters. Indeed, in the literature, only a few authors have addressed its evaluation (Falkenmark, 2013; Pellicer-Martínez and Martínez-Paz, 2016b; Salmoral et al., 2017; Veettil and Mishra, 2016), although the importance of WS_{green} was already underlined by Savenije (2000). In this study, the CWU_{env} was evaluated as green water used by forest, bushes, shrubs and pasture (D'Ambrosio et al., 2017b). Meanwhile, the CWU_{unprod} was evaluated as the evapotranspiration from set-aside land (i.e., fallow land) and urbanised areas.

3.7.2 BLUE WATER SCARCITY

Unlike the WS_{green} concept, the WS_{blue} index had been assessed by several authors (Cazcarro et al., 2015; de Miguel et al., 2015; Zeng et al., 2013, 2012; Zhuo et al., 2016; Zoumides et al., 2014).
Blue water scarcity (WS_{blue}) is a measure of the environmental sustainability of the WF_{blue} in a catchment. It is the ratio of the total WF_{blue} in the catchment ($\sum WF_{blue}$) to the blue water availability (WA_{blue}):

$$WS_{blue} = \frac{\sum WF_{blue}}{WA_{blue}} \qquad \text{eq.(31)}$$

According to de Miguel et al. (2015), the WS_{blue} is classified into four levels: low (<1), moderate (1–1.5), significant (1.5–2) and severe (>2) water scarcity.

The WA_{blue} (m^3 $month^{-1}$) was assessed through the following equation:

$$WA_{blue} = R_{nat} - EFR \qquad \text{eq.(32)}$$

, where R_{nat} is the natural runoff in the catchment, estimated by summing the measured runoff (Q_{MP}) to the water withdrawal for irrigation (I), and subtracting the total WWTP discharge (WW). Meanwhile, EFR is the environmental flow requirement, that was set to be equal to Q_{MP}, if Q_{MP} was lower than 0.05 m^3 s^{-1}, and to 0.05 m^3 s^{-1}, if Q_{MP} was greater than 0.05 m^3 s^{-1}, as established by the river basin authority (Distretto Idrografico dell'Appennino Meridionale, 2016); however, differently from this assumption, many authors have assumed that EFR accounts for an 80% share of the R_{nat} (EFR^C) (de Miguel et al., 2015; Hoekstra et al., 2012; Zeng et al., 2012; Zhuo et al., 2016). For comparison, EFR^C was also used for calculation, and $WS_{blue}{}^C$ was calculated thus (D'Ambrosio et al., 2017b).

3.7.3 WATER POLLUTION LEVEL

The environmental sustainability of the WF_{grey} was conducted using the WPL indicator, which is calculated by dividing the total WF_{grey} ($\sum WF_{grey}$) by the actual runoff from the catchment (R_{act}):

$$WPL = \frac{\sum WF_{grey}}{R_{act}} \qquad \text{eq.(33)}$$

In this study, the R_{act} (m^3 yr^{-1}) was set equal to the measured runoff (Q_{MP}), less WW discharge (D'Ambrosio et al., 2017b).

The WPL can be considered as the fraction of the waste assimilation capacity consumed (Hoekstra et al., 2011). It can take values from 0 to above 1. A WPL greater than 1 indicates that the WF_{grey} is unsustainable, since the capacity to assimilate the existing pollutant load of the river has been surpassed. Conversely, WPL values lower than 1 indicate that there is enough water to dilute the pollutant load to below the maximum acceptable concentration at the basin scale (Liu et al., 2012).

The WPL was assessed considering both WF_{grey} and $WF_{grey}{}^C$.

4 STUDY AREA

4.1 MEDITERRANEAN REGIONS

Mediterranean regions lie in a transition zone along a climatic gradient between temperate and desert climate region and are affected by interactions between mid-latitude and tropical processes (Bonada and Resh, 2013; Giorgi and Lionello, 2008).

For each Mediterranean region, the geographical limits depend on the climate classification system used.

The most frequently used world climate classification map is that of Köppen, whose latest version (Köppen-Geiger map) was published in 1961 (Köppen and Geiger, 1961). The classification is based on a combination of monthly surface air temperature and precipitation and identifies 30 climate regimes. Thus, according to this classification, the Mediterranean climate would be included within the ‘‘warm temperate climate with dry and hot summer’’ and the “warm temperate climate with dry and warm summer’’ climate typology, that is the ‘‘Csa’’ and “Csb” type, respectively (Kottek et al., 2006) (Fig. 4).

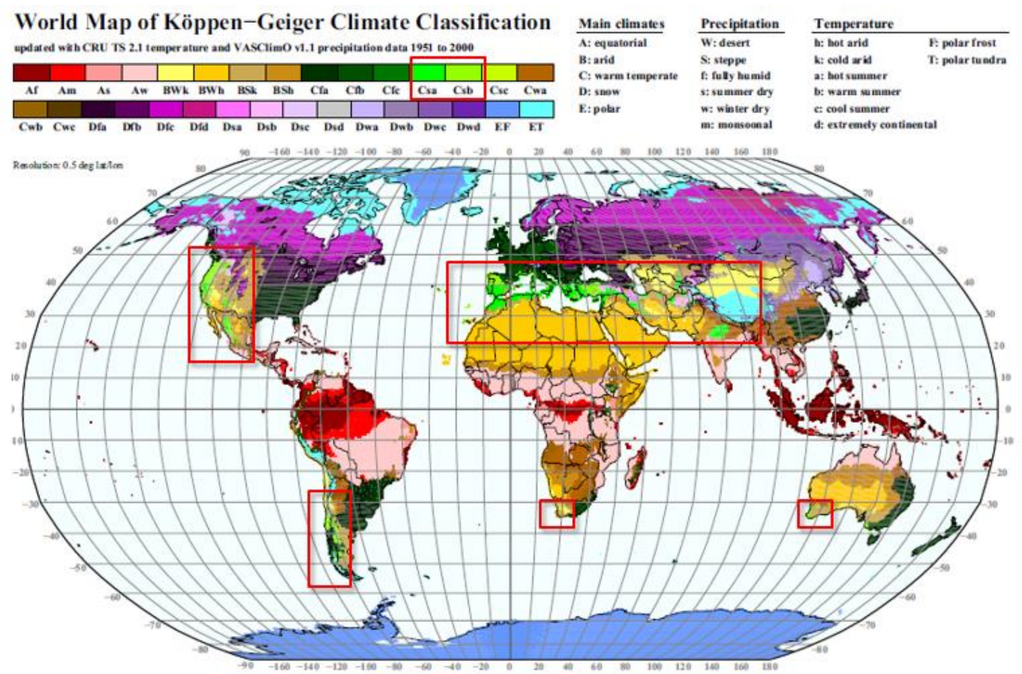

Fig. 4: Location of Mediterranean Regions (red rectangles) according to Köppen-Geiger map (modified from Kottek et al., 2006)

This Mediterranean climate occupies less than 5% of the Earth’s surface, and lies between 32° and 40° N and S of the Equator, and are located in the south or west side of these continents (Aschmann, 1973a da Bonada and Resh, 2013). It occurs in five different regions: the

Mediterranean Basin, coastal California, central Chile, the Cape region of South Africa, and the southwest and southern parts of Australia.

The climate of the Mediterranean is mild and wet during the winter and warm/hot and dry during the summer. It is typically defined by the high seasonality in the precipitation and temperature patterns that occur annually. The annual precipitation ranges generally from 300 to 900 mm/year, with most rainfall occurring during the winter (Miller, 1983 da Bonada and Resh, 2013). Summer storms can be also frequent especially in the southern hemisphere (Cowling et al., 2005 da Bonada and Resh, 2013). At least 65% and often 80% or more of the rain falls in the three winter months, with most of the precipitation often falling during a few storm events (Gasith and Resh, 1999).
Meanwhile, winter temperatures in Mediterranean Regions are generally between 7–13 °C with infrequent frosts and snow, whereas summers have a mean temperature of 14–25 °C (Bonada and Resh, 2013).
Future climate change scenarios have identified the Mediterranean region as a climate change hot spot. They predict a rise in temperatures, an exacerbation of drought conditions, a growing rate of desertification and an increase of the occurrence of extreme events such as floods, heat waves, and wildfires (IPCC, 2007).

Because of the strong influence of the climate, faunal and floral similarities among the Mediterranean Regions of the world have long been recognized from the mid-1700s (Di Castri, 1981 from Bonada and Resh, 2013). In particular, most authors agree that this biological similarity is due to the duration of the summer dry period and the persistence of typical low but not freezing winter temperature (Aschmann, 1973a; Bonada and Resh, 2013; Miller, 1983; Stella et al., 2013). Olive groves, vineyards, orchards, and durum wheat crops are frequently cultivated in Mediterranean regions.

Moreover, the climate exerts a great influence also on the river network. Indeed, Mediterranean rivers have flow regimes that reflect the precipitation patterns of the Mediterranean climate. They are characterized by different levels of hydrological connectivity between seasons, with an expansion phase in the wet period (i.e., autumn– winter) and a contraction phase in the dry period (i.e., spring-summer) (Bernal et al., 2013; Bonada et al., 2007b; Skoulidis et al., 2017).
During the dry period, the lack of precipitation and the high evapotranspiration rate result in a steady reduction of the longitudinal, lateral, and vertical flow connectivity. This reduction process leads to a sequence of disconnected pools that in certain extreme circumstances can also disappear, leaving dry riverbeds. Conversely, during autumn-winter period, precipitation restores longitudinal, lateral and vertical flow connectivity, and disconnected pools disappear. In small and steep basins, this flow expansion can occur with a very short time lag because of intense storms that often lead to intense flash floods from late summer to autumn (Camarasa-Belmonte & Segura- Beltra´n, 2001; Gallart et al., 2012; Llasat et al., 2010).
Thus, in Mediterranean regions, temporary rivers (defined as rivers that cease to flow at the surface for some time of the year) are the dominant freshwater type (Tockner et al., 2009; Bonada and Resh, 2013). Depending on the specific flow regime, temporary rivers can be classified, as intermittent (if cease to flow seasonally or occasionally), ephemeral (if flow only in response to

precipitation or snowmelt events) or episodic (if carry surface water only during very short periods, primarily after heavy rainfall events) (McDonough et al., 2011; Arthington et al., 2014). Temporary rivers are not exclusive to med-regions, accounting for 50% of the total length of the global river network including low order streams (Datry et al., 2014a). However, the hydrological regime of Mediterranean temporary rivers is considered to be more predictable than those of other climate regions, since the timing of drying and flooding is very foreseeable (Williams, 2006). Conversely, the intensity of drying and flooding is unpredictable: some years have longer dry periods than others or have a higher frequency of floods (Resh et al., 2013).

Summing up, hydrological regimes in Mediterranean rivers are strongly determined by three dimensions: seasonal (i.e., predictable occurrence of drying and flooding), interannual (i.e., the intensity of drying and flooding can change from year to year), and spatial (i.e., a mosaic of flow connectivity can be present, even within a small section of stream).

Mediterranean rivers are subjected to many types of disturbances, both natural and human-induced (Skoulikidis et al., 2017). Seasonal floods and droughts can be considered as natural disturbances, as well as fire, that is another predictable disturbance in Mediterranean regions, since mainly occurs in summer when riparian vegetation are dry (Verkaik et al., 2013).
Human-induced disturbances are numerous and derived from agriculture, livestock, industrial practices, human population growth and other accompanying activities. According to Sabater et al. (2009), "*people in arid and semi-arid regions have the least respect towards rivers"* especially when the rivers are often dry. This is particularly evident in urban areas, where they have been frequently covered by roads (e.g. the "Ramblas" in Barcelona, Spain), car parking areas, drains for sewage effluents, legal and illegal constructions. Another cause of water consumption and degradation is agriculture, due to the use of large volumes of water for irrigation, and of pesticides and fertilisers (Chouchane et al., 2015; Rulli and D'Odorico, 2013; Ventura et al., 2008). Indeed, in most countries of the Mediterranean Basin, irrigation water is mainly obtained from rivers and streams, covering 64% (France) to 100% (Portugal) of the demand (INAG, 2001).

Therefore, seasonal flooding and drying, anthropogenic impacts, population growth, and the consequent competition between water needs for the environment, agriculture and domestic/industrial use, make these systems the most diversely stressed of any riverine habitat in any climate type worldwide (Bonada and Resh, 2013; Skoulikidis et al., 2017).

Until recently, Mediterranean rivers have been considered as impoverished or even biologically-inactive ecosystems (De Girolamo et al., 2017a; De Girolamo et al., 2017b; De Girolamo et al., 2015a; Skoulikidis et al., 2017). A low economic value was generally attributed to temporary streams, and limited availability of resources for research and development were allocated.
Therefore, information about their spatial extent, hydrological regime and about their ecology are scant, and their conservation and management are ineffective.

4.2 CASE STUDY

Two different study areas representative of Mediterranean regions, in terms of climate, soil uses and data availability, were analysed. In particular, Candelaro, Carapelle and Cervaro watersheds have been used as case studies for the hydrological regime characterization. Meanwhile, the instrumented catchment of the Celone has been analysed for riverine export estimation, nitrogen balance and total WF assessments.

4.2.1 CANDELARO, CARAPELLE AND CERVARO CATCHMENTS

The study area includes the Candelaro, Carapelle and Cervaro catchments which are located in southeast Italy (D'Ambrosio et al., 2017a). The catchments have total drainage areas of 2300 km^2, 990 km^2 and 775 km^2 respectively (Fig. 5).

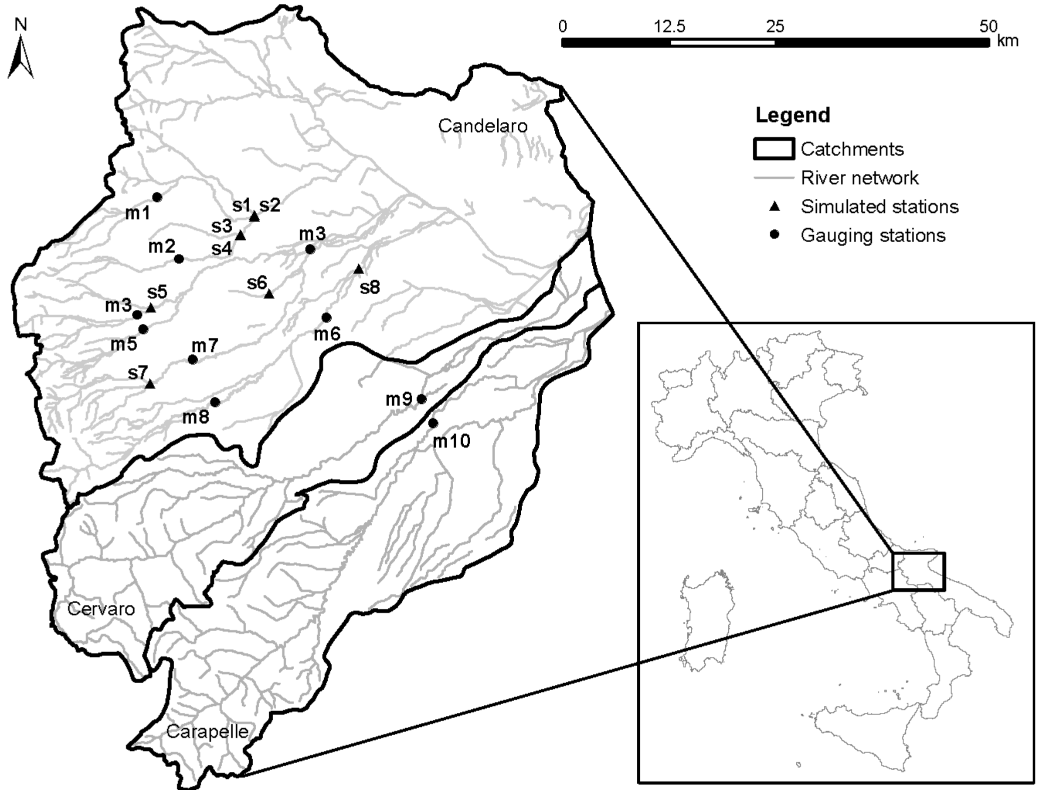

Fig. 5: Study area: Candelaro, Cervaro and Carapelle catchments (D'Ambrosio et al., 2017a)

The mean elevation of each respective catchment is 195 m (ranging from 0-1142 m), 287 m (0-1085m) and 352 m (0-1095m) above sea level. The catchment soil types are related to their lithology. Generally, soil textures vary from sandy-clay-loam to clay-loam or clay in each catchment. The elevation and slope exposure (orography) in each catchment affects rainfall total and patterns at the event time scale. Although rainfall is concentrated in autumn and winter, it is unevenly distributed across the catchments and can be intense and short in duration. Intensive agriculture is the main economic activity in the plain areas. The main farm products are durum wheat, tomatoes, sugar beet, olives and vineyard grapes. In the mountainous parts of each

catchment, where morphology is more irregular, natural and man-made forests and pastures are common.
During and soon after a rainfall event, the stream flow regime changes rapidly. It closely follows changes to the precipitation regime.
River networks are intermittent in character, with a pattern of zero or low flow and the concentration of surface water into isolated pools along the river during the summer months. Their hydrological regime is characterised by frequent flash flood events from June to September. A flood event typically lasts a few hours, with the hydrograph showing a steep rising limb and short rainfall-runoff lag time. Conversely, the winter flow hydrograph shows a mild falling limb depending on antecedent soil moisture, and the intensity and duration of the rainfall event.

4.2.2 CELONE CATCHMENT

The second study area is the upper basin of the Celone River that covers a drainage area of approximately 72 km^2 (Fig. 6) (D'Ambrosio et al., 2017b). The catchment is located in the Puglia region in southern Italy, and is a tributary of the Candelaro River. It is representative of a larger area including the Monti Dauni where all the tributaries of the Candelaro river have their origin and for this reason data collected here are important for the management of the whole Candelaro river basin.

The Celone watershed is characterised by a mean elevation of 500 m above sea level, ranging from 150 m to 1150 m. The main course of the Celone River is about 28 km long; it flows northeast, and enters the Capaccio Reservoir, characterised by a full capacity of 25.82 Mm^3 (on 12th April, 2016 the water volume was 17.0 Mm^3).

Soils are related to lithology, and here show a texture varying from clay, to clay-loam and sandy-clay-loam (D'Ambrosio et al., 2017b). The depth of the soils is highly variable, the hilly and mountainous parts of the study area consist of moderately deep soil (less than 1 m), while the plain part of the catchment comprises deep soils (1.5-2 m). Considering the ACLA 2 (2001) soil maps, six different soil layers, and two hydrological soil groups (C, D), can be identified (Fig. 6). The geology of the area is quite complex; in the upper part of the basin (the study area), the major bedrock lithological units are grey-blue clay and flysch formations (Flysch della Daunia), while the lowland is characterised by alluvial deposits (Ippolito et al., 1958).
As a result of the geological structure of the area, seepages are limited to the lowlands, and groundwater resources are significant only in the alluvial aquifer. In the study area, the geological formations have a very low permeability, so the aquifer is not significant. Therefore, the Celone catchment can be considered hydraulically isolated (D'Ambrosio et al., 2017b).

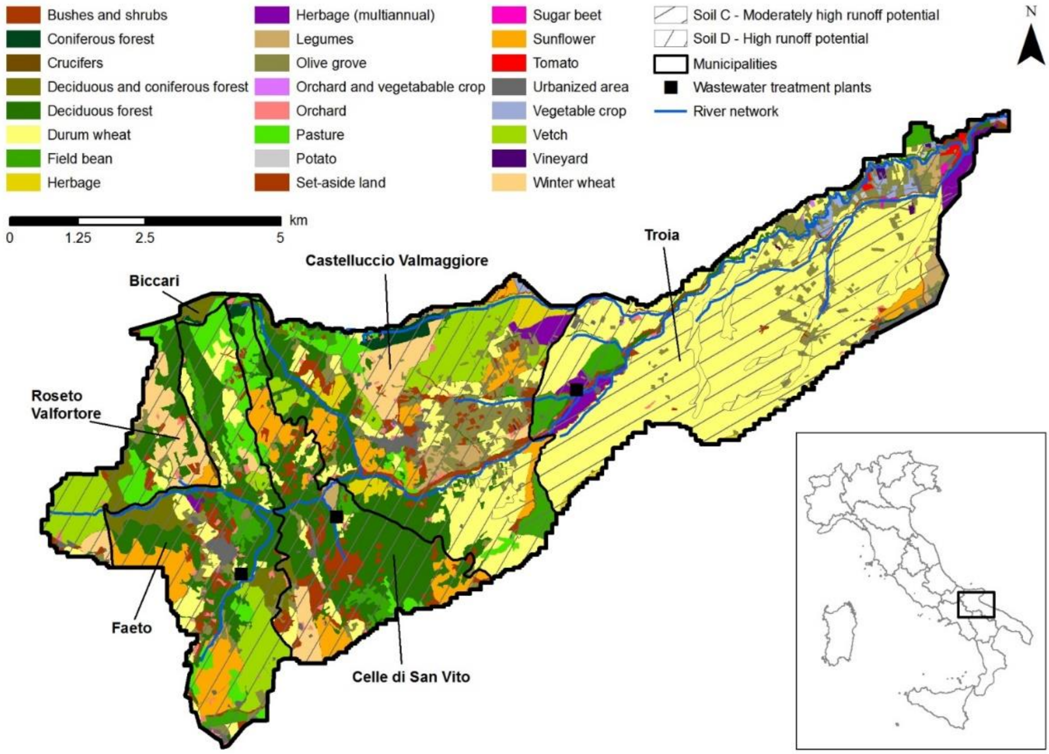

Fig. 6: Study area: Celone river basin (D'Ambrosio et al., 2017b)

The river system consists of the main stream (Celone) and several primary and secondary order tributaries. In the hilly zone, the channel is naturally confined, with steep gradients and unstable banks. Only in the alluvial plain, coarser materials deposit and the river assumes a braided form, large and with water level relatively shallow. At the lower elevation, the river has a sinuous course with riparian vegetation along the channel.
The river system has a typical Mediterranean semi-arid regime, with a seasonal pattern of drought and flash floods, which have an important role in nutrient delivery and loss (De Girolamo et al., 2017a, 2017b, 2012a). According to the national Decree of the Ministry of the Environment n. 131/2008 (D.M. 131/2008, 2008), this river body is defined as an ephemeral river (an ephemeral stream is a temporary river with continuous flow conditions during less than 8 months per year).

The climate of the study area is typically Mediterranean, with warm, dry summers and wet winters (D'Ambrosio et al., 2017b). The mean monthly temperature range (1989-2012) is between 4.3°C in January and 22.1°C in August in the upper part of the basin (Faeto), and from 7°C in January to 25.5°C in August in the lowland area (Troia). Rainfall, mostly concentrated in autumn and winter (from November to May), shows great spatial variability, and often occurs as high-intensity and short-duration events. The mean annual rainfall (1950-2012) is 820 mm in the mountainous area (Faeto) and 638 mm in the hilly-plain area (Troia). Generally, during the dry season, rainfall is concentrated in a few events. These rainfall characteristics exercise a great influence on the flow regime and, in general, on processes such as erosion, and sediment and nutrient delivery; however, the study period (July 2010 – June 2011) is representative of the historical hydrological conditions recorded in the basin, although it was wetter than the average conditions (Table 6).

Table 6: Rainfall data recorded in the catchment

Rainfall (mm)													
Period	**Jul**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**June**	**Year***
FAETO GAUGE (lat. 41° 19' 19.45" N; long. 15° 9' 47.51" E)													
2010-2011	119.8	1.2	78.8	139.0	190.0	98.6	84.2	75.6	158.0	119.2	78.4	50.6	1193.4
1950-2012	32.5	35.6	55.9	75.3	100.1	105.6	88.7	72.7	78.9	84.2	51.3	38.8	822.3
TROIA GAUGE (lat. 41° 21' 41.26" N; long. 15° 18' 34.52" E)													
2010-2011	94.6	0.2	47.6	107.0	106.8	53.8	67.4	34.6	90.6	59.0	50.8	50.0	762.4
1950-2012	33.1	31.9	45.7	65.8	74.8	75.8	65.8	48.3	56.8	63.7	42.7	40.2	640.9

* It is a 12-month period that starts on July

The main economic activity in the area is traditional, extensive agriculture: about 70% of the watershed land resources are devoted to agricultural uses. Durum wheat (in rotation with set-aside land, vetch and field bean) (44.8%) and olive trees (7.5%) are the main cultivations. Natural deciduous forest (mainly *Quercus spp.* and *Fagus sylvatica L.*) and coniferous plantations are present (20.1%), especially in the mountainous area (D'Ambrosio et al., 2017b). Other areas in the catchment reserved for nature are pasture (5%) and riparian vegetation (3.3%). The urban area is limited to 2.6%, and three small villages fall within the watershed. Wastewater is treated in three treatment plants (about 3,000 EI), discharging into the river.

Cattle- and sheep-breeding is another relevant activity in the area. Indeed, 560, 2,760 and 820 are the approximate number of cattle, sheep and pigs, respectively (ISTAT, 2010). Most of them are still managed in a traditional, extensive way, since they are allowed to freely move on pasture. About 25 horses and 90 rabbits are also present; in addition, there are 240,000 chickens in the area, 99% of them living in a battery farm. Manure is spread to fertilise crops.

5 RESULTS

5.1 HYDROLOGICAL REGIME CHARACTERIZATION

5.1.1 PCA OF HYDROLOGICAL INDICES

Prior to performing PCA, redundant indices were removed. As a result, only 18 of the 37 HIs were included in the multivariate analysis (D'Ambrosio et al., 2017a). The indices included were: MAJ, MAMar, MAJN, MAN, DL4, DL5, DH1, DH4, DH5, DL6, ML1, FL1, FH1, RA2, RA3, MF, SD6 and FI_RB.

Variables which were highly correlated i.e. correlation coefficients greater than 75% or exhibited no variance were rejected. There were 19 of these variables. For example, the variables DL1, DL2 and DL3 showed no variance because they were always equal to zero. For the same reason, none of indices of group 3 (TL1, TH1) were retained because during the sampled years these dates fell in the same approximate periods for all the stations. Conversely, the indices of group 1 were highly correlated with each other, hence only MAJ, MAMar, MAJN, MAN were considered. The data matrix dimensions were reduced from 10×37 to 10×18. In Table 7 the loading values of the hydrological indicators (HIs) are shown. Three factors (PCs) were calculated, explaining up to 82% of the total variance.

Table 7: Principal Component Analysis results. Loading values greater than 0.28 emboldened (D'Ambrosio et al., 2017a)

Group	HIs	ANALYSIS (81.6%)		
		PC1	**PC2**	**PC3**
1	MAJ	0.266	0.143	**0.323**
	MAJn	0.021	**0.446**	0.075
	MAMar	0.184	-0.213	**0.407**
	MAN	**-0.308**	-0.076	-0.018
2	DH1	0.073	-0.236	0.033
	DH4	0.197	-0.243	**0.385**
	DH5	0.176	**-0.318**	**0.360**
	DL4	-0.260	0.106	0.207
	DL5	-0.202	0.262	0.275
	DL6	**0.274**	-0.138	-0.198
	ML1	-0.239	0.142	0.180
4	FH1	-0.211	**-0.371**	-0.069
	FL1	**-0.308**	0.079	0.254
5	FI_RB	-0.175	**-0.296**	**-0.317**
	MF	**-0.312**	0.035	0.200
	RA2	**-0.304**	-0.045	-0.087
	RA3	-0.277	-0.212	0.069
	SD6	-0.218	**-0.339**	0.183
Eigenvalues	-	8.30	3.71	2.68
% variance explained	-	46.1	20.6	14.9

The first Principal Component (PC1) accounting for 46% of the total variance was mainly associated with the rate and frequency of water condition changes (MF, RA2) and with the low flow indicators: mean flow in November (MAN), number of zero days (DL6) and low pulse counts (FL1) (D'Ambrosio et al., 2017a). The second Principal Component (PC2), accounting for 21%, was dominated by high loading values of indicators associated with the following water conditions: mean flow in June (MAJN), annual maximum 90-day mean (DH5) and high pulse count (FH1), and frequency of water condition changes, flashiness and predictability (FI_RB, SD6). The third Principal Component (PC3) accounting for 15% of the total variance, showed high loading values for flow magnitude for wet months January and March (MAJ, MAMar), magnitude of annual maxima 30-day and 90-day duration (DH4, DH5) and flashiness (FI_RB).
The difference between stations within the study area was also investigated. Fig. 7 shows the positioning of the 10 gauging stations in the new orthogonal coordinate system (PC1, PC2).

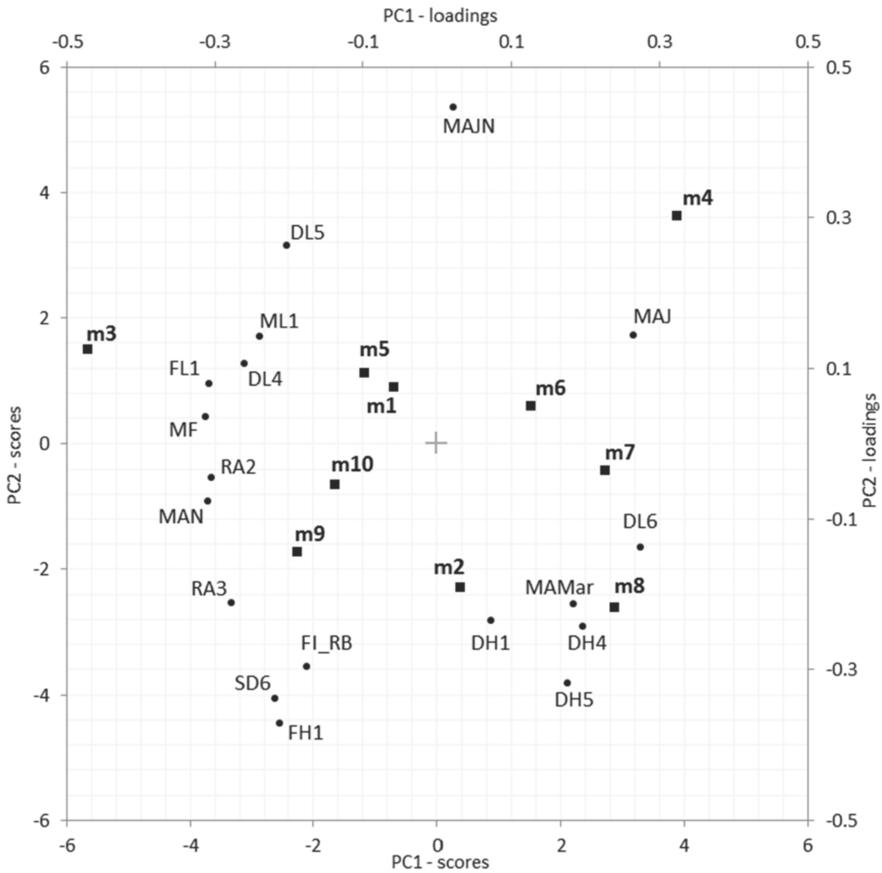

Fig. 7: PCA results. Biplot (PC1, PC2) (D'Ambrosio et al., 2017a)

A difference between the gauging stations emerges from the biplot obtained from the PCA. Station m3 shows a lower value of PC1, whereas m4 has higher scores for both PC1 and PC2. The score of the m3 gauging station along the first PC1 is dominated by higher values of the FL1 and MF1 indices. The scores for station m4 are mostly influenced by the higher values of MAJ and MAJN indices between all stations.

5.1.2 REGRESSION MODELLING, INDEX PREDICTION AND RIVER TYPE CLASSIFICATION

Two regression analyses were performed in order to identify the most statistically significant relationship between each of the selected indices (MAJ, MAMar; MAJN; DH4; DH5; DL6; FH1; RA2; FI_RB; MF and SD6) and the key catchment characteristics (D’Ambrosio et al., 2017a). Table 8 shows values of the catchment characteristics for all the analysed stream sites.

Table 8: Analysed catchment characteristics. A is the catchment area; E is the station elevation; Z is the mean catchment elevation; S is the mean catchment slope; MRA is the mean annual rainfall; UDS1, UDS2 and UDS3 are artificial surfaces, agricultural areas and forest and semi-natural areas respectively; K is the hydraulic conductivity; AWC is the Available water content (D’Ambrosio et al., 2017a)

Station	A (km^2)	E (m)	Z (m)	S (%)	MRA (mm)	UDS1 (%)	UDS2 (%)	UDS3 (%)	K (mm/hr)	AWC (%)
m1	52.68	93.45	197.63	3.57	648.74	0.00%	100.00%	0.00%	0.55	0.11
m2	57.23	113.77	285.63	4.44	662.96	1.15%	94.24%	4.61%	1.29	0.11
m3	433.30	42.01	291.01	3.97	598.33	1.50%	90.85%	7.65%	0.45	0.11
m4	55.35	180.00	422.41	6.36	682.48	0.59%	84.48%	14.93%	0.29	0.11
m5	41.50	186.31	432.64	7.33	674.88	0.00%	86.00%	14.00%	0.32	0.11
m6	214.70	64.14	342.78	4.36	595.92	0.37%	88.43%	9.79%	1.39	0.11
m7	95.43	173.49	461.50	6.15	723.99	0.00%	83.74%	16.26%	0.37	0.11
m8	84.01	192.63	542.50	7.62	732.59	0.43%	76.52%	23.05%	0.97	0.11
m9	660.86	57.31	410.34	5.69	694.15	2.12%	82.96%	14.92%	1.01	0.11
m10	720.47	58.00	377.53	5.28	612.52	0.74%	90.26%	9.00%	0.57	0.11
s1	36.76	53.38	105.70	1.51	604.45	2.31%	97.69%	0.00%	0.14	0.10
s2	142.86	53.45	190.68	2.76	656.82	1.08%	97.07%	1.85%	1.47	0.11
s3	40.15	61.80	128.93	2.13	555.67	0.47%	99.53%	0.00%	1.59	0.11
s4	97.08	61.95	223.71	3.20	704.55	1.39%	95.89%	2.72%	1.49	0.11
s5	39.70	41.04	99.25	0.83	505.64	0.14%	99.82%	0.00%	1.27	0.11
s6	35.56	67.95	114.66	1.30	555.67	4.06%	95.94%	0.00%	0.51	0.12
s7	37.67	157.90	359.94	5.07	808.21	0.00%	92.44%	7.56%	0.65	0.12

All streamflow sites were considered in this analysis. The matrix of Spearman rank correlation coefficients of the catchment features is shown in Table 9.

After checking the degree of correlation amongst the aforementioned catchment characteristics, the number was reduced to seven. Mean catchment elevation (Z), percentage of artificial surfaces (UDS1) and of forest and semi-natural areas (UDS3) were found to be redundant, and were not considered as independent variables.

The selected HIs and the catchment features overcame the four tests for Gaussian normality i.e. Shapiro-Wilk, Anderson-Darling, Lilliefors and Jarque-Bera.

Only eight of the selected HIs (MAMar, DH4, DH5 DL6, RA2, FI_RB, MF and SD6) were found to be significant with respect to the linear model. In particular, the R2 values ranged from approximately 0.65 to 0.90 and the p-values ranged from 0.000 to 0.004.

The scatterplots of predicted vs. observed values with the confidence interval at 95% significance, show that all the points fall within the confidence interval with the exception of a single point for the MAMar variable (D'Ambrosio et al., 2017a). Analysis of the residuals for all the linear models shows that all the residual distributions are normal according to the four Gaussian normality tests.

The RMAE values associated to the multi-regressive linear models are included in the range of 0.13– 0.69. It is noteworthy that there is a group of variables which are well described by the linear model. In fact, the RMAE value for those variables (FI_RB; MAMar; DH5; DH4) ranges from about 13% to 27%. This means that for the variables considered, the error produced by the model is a small fraction of the magnitude order of the observed value itself. Hence, it can be concluded that the linear model is able to describe the variables FI_RB, MAMar, DH5 and DH4.

Table 9: Matrix of Spearman correlation coefficients of the catchment features (D'Ambrosio et al., 2017a)

	A (km^2)	E (m)	Z (m)	S (°)	MAR (mm)	UDS1 (%)	UDS2 (%)	UDS3 (%)	K (mm/h)	AWC (%)
A (km^2)	1.00	-0.43	0.19	0.13	-0.05	0.18	-0.24	0.27	0.41	0.12
E (m)	-0.43	1.00	0.68	0.71	0.62	-0.69	-0.54	0.59	-0.30	0.01
Z (m)	0.19	0.68	1.00	0.98	0.72	-0.57	-0.93	0.98	-0.31	0.01
S (°)	0.13	0.71	0.98	1.00	0.72	-0.57	-0.89	0.95	-0.34	-0.02
MAR (mm)	-0.05	0.62	0.72	0.72	1.00	-0.45	-0.63	0.67	-0.18	-0.11
UDS1 (%)	0.18	-0.69	-0.57	-0.57	-0.45	1.00	0.30	-0.46	0.13	0.11
UDS2 (%)	-0.24	-0.54	-0.93	-0.89	-0.63	0.30	1.00	-0.97	0.31	-0.01
UDS3 (%)	0.27	0.59	0.98	0.95	0.67	-0.46	-0.97	1.00	-0.30	-0.05
K (mm/h)	0.41	-0.30	-0.31	-0.34	-0.18	0.13	0.31	-0.30	1.00	-0.03
AWC (%)	0.12	0.01	0.01	-0.02	-0.11	0.11	-0.01	-0.05	-0.03	1.00

Table 10 shows the following:

- The dependent variables with the goodness-of-fit value and the p-value of the related linear multi-regressive model.
- The independent variables significantly involved in each model with the related p-values.
- The explicit model equation for each linear model.

The remaining variables have an RMAE of approximately 50% (DL6; RA2; MF) or larger, for SD6 which indicates that the linear model is a poor representation for such variables. Given the positive results of the normality tests, a scarce RMAE result can be interpreted in two ways: i)

the white noise in a variable is significantly large (high uncertainty in the data) and ii) the behaviour of a variable could be non-linear with respect to the regressors. This last consideration enables the use of second-order polynomials.
In contrast to the linear model, all the HI results were highly significant with the second order model. The goodness-of-fit values ranged from 0.91 to 0.98 and the RMAE was included in the interval 0.06 and 0.19. The value of R^2 was elevated which could be explained by the large number of regressors. However, some variables which were not significant with respect to the linear model, became significant. These variables are MAJ MAJN and FH1. This indicates that the linear model not being a proper descriptor for such variables could be a plausible hypothesis. The p-values for the four normality tests on the second order model residuals show inhomogeneous behaviour in the residual distributions.

Table 10: Linear equations for the HIs fitting linear model and main statistical indicators. A is for the catchment area, E is for the gauging station elevation, S is for the mean catchment slope and MAR is for the mean annual rainfall (D'Ambrosio et al., 2017a)

	Intercept	A	E	S	MAR
	DH4 = -0.03182 + 0.09180*S + 0.00006*MAR (R^2 = 0.902, model p-value < 0.0001)				
Coefficient	-0.03182	-	-	0.09180	0.00006
p-value	0.000	-	-	0.002	0.000
	DH5 = -0.06898+0.04183*A+0.05319*S +0.00003*MAR (R^2 = 0.861, model p-value < 0.0001)				
Coefficient	-0.06898	0.04183	-	0.05319	0.00003
p-value	0.006	0.015	-	0.009	0.008
	MAMar = -0.12810 + 0.05080*A + 0.03687*E (R^2 = 0.811, model p-value < 0.0001)				
Coefficient	-0.12810	0.05080	0.03687	-	-
p-value	<0.0001	<0.0001	<0.0001	-	-
	FI_RB = 11.39640 - 4.79446*A - 3.28183*E + 0.00183*MAR (R^2 = 0.699, model p-value = 0.001)				
Coefficient	11.39640	- 4.79446	-3.28183	-	0.00183
p-value	0.000	0.000	0.001	-	0.003

It is noteworthy that for MAJ and FH1, both insignificant with respect to the linear model, the behaviour of the residuals is normal. This confirms the non-linearity hypothesis. Furthermore, the residuals for RA2, MF and partly SD6, which behaved poorly with the linear model, show a normal distribution. In contrast, the variables which perform well with the linear model show a marked departure from normality. This suggests the presence of possible over-fitting. A plausible interpretation of these results is that some HIs are correctly described by the linear model and others have more complex relationships with the regressors (D'Ambrosio et al., 2017a).
The following scatterplots show the best results for all considered variables for predicted vs. observed according to a second order model. As expected from the high values of R^2 and RMAE, the scatterplots show a strong relationship between predicted and observed values (Fig. 8).

The second order model, which is suggested for MAJ, MAJN, DL6, FH1, RA2, MF and SD can be expressed by the following general equation:

$$\begin{aligned}Y = {} & pr1 + pr2*S + pr3*PMA + pr4*\text{arcsine-square root}(UDS2) + \\ & pr5*\ln(K) + pr6*AWC + pr7*\text{boxcox}(A) + pr8*\text{boxcox}(E) + pr9*S\text{^}2 + \\ & pr10*PMA\text{^}2 + pr11*\text{arcsine-square root}(UDS2)\text{^}2 + pr12*\ln(K)\text{^}2 + \\ & pr13*AWC\text{^}2 + pr14*\text{boxcox}(A)\text{^}2 + pr15*\text{boxcox}(E)\text{^}2\end{aligned} \qquad \text{eq.(34)}$$

The values of the polynomial parameters within the second order model equation are reported in Table 11.

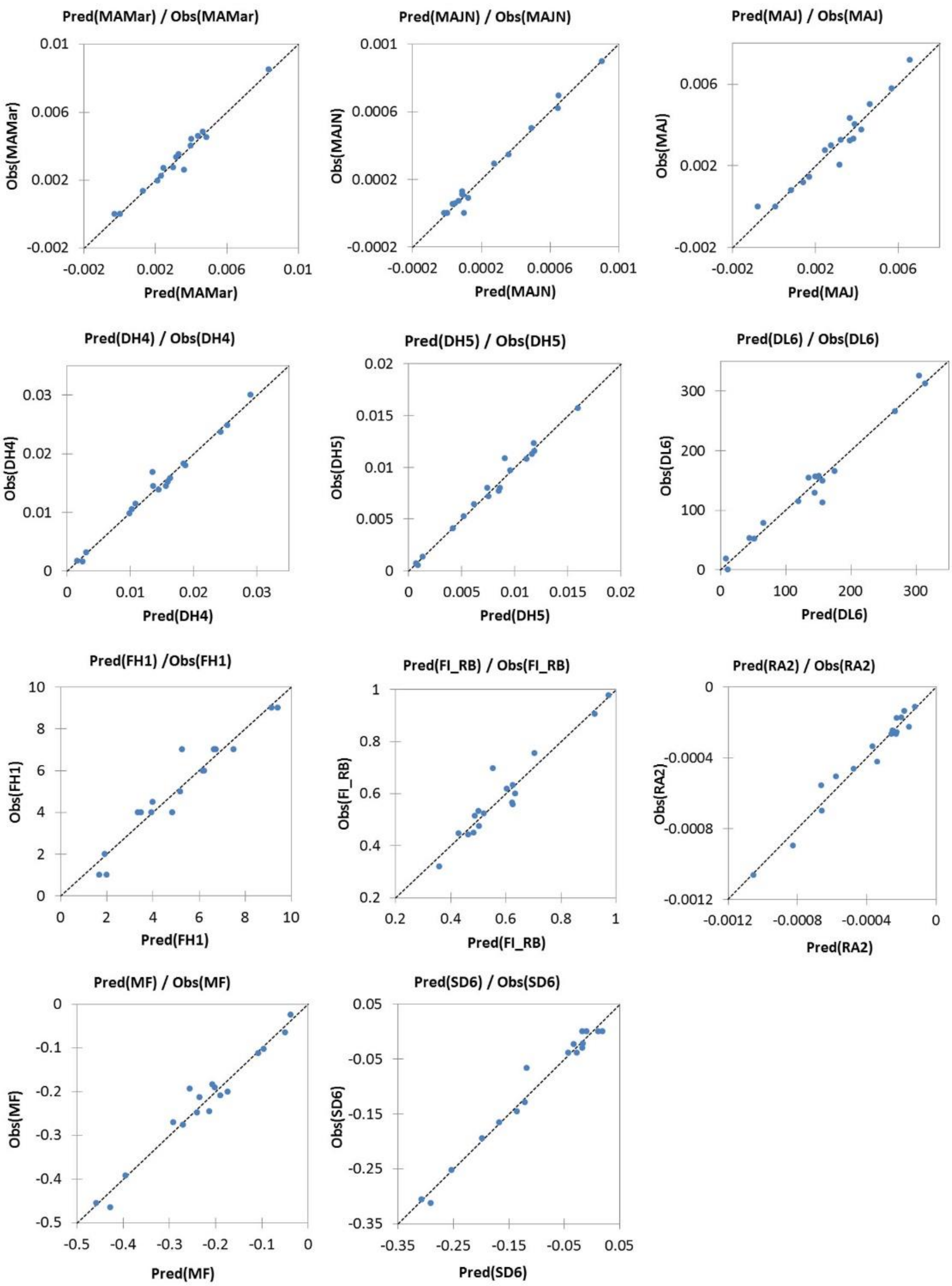

Fig. 8: Scatterplots of predicted vs. observed values for the second order regression model (D'Ambrosio et al., 2017a)

Table 11: Second order regression model: MAJ, MAJN, DL6; FH1; RA2, SD6 and MF polynomial parameters. SD6 and MF are expressed as box-cox transformation (D'Ambrosio et al., 2017a)

Parameter	MAJ	MAJN	DL6	FH1	RA2	SD6	MF
pr1	2.912	0.377	16726.191	-4880.786	-0.104	-78.559	-160.978
pr2	0.043	0.028	-9303.389	79.999	-0.004	0.753	12.838
pr3	0.000	0.000	-8.914	-0.046	0.000	0.004	0.006
pr4	-0.293	-0.057	3431.039	388.026	-0.006	6.033	-0.011
pr5	0.009	0.001	23.985	-11.346	0.000	-0.032	-0.163
pr6	-18.110	-0.624	26380.151	-4998.207	-1.476	-111.300	-79.804
pr7	-2.133	-0.362	-27531.606	5556.187	0.130	135.292	218.403
pr8	-0.665	-0.106	-2178.569	1705.960	0.124	-6.876	31.617
pr9	-0.601	-0.178	37007.985	589.730	0.091	27.695	-36.038
pr10	0.000	0.000	0.006	0.000	0.000	0.000	0.000
pr11	0.113	0.022	-1271.764	-146.128	0.003	-2.164	-0.054
pr12	0.008	0.001	-2.862	-10.568	0.000	-0.054	-0.114
pr13	86.999	3.620	-170153.170	16947.040	6.921	511.357	362.854
pr14	0.868	0.139	11403.142	-2165.723	-0.051	-52.402	-85.575
pr15	0.209	0.030	1346.972	-509.857	-0.038	1.054	-10.418

5.1.3 CLASSIFICATION

In the plot SD6 vs. MF, most of the reaches are classified as P or I-P (Fig. 9). This classification represents an average over the study period (D'Ambrosio et al., 2017a). However, it could change from year to year due to inter-annual variability of the hydrological regime recorded in the study area. Hence, a water body which is defined in the long term as an I-P river can show a hydrological gradient from P to Intermittent Dry during one-year periods. In the plot, the grey triangle shows the area where the metrics are incompatible. The red lines show an approximate separation between the regime types.

The river reaches are represented in the plot using the indices derived from measured flow data (Fig. 9a) and the predicted values (polynomial regression model) based on catchment characteristics (Fig. 9b). Fig. 9b shows when using the regression equations based on the catchment characteristics, the river reach classification remains the same as that based on long-term flow data.

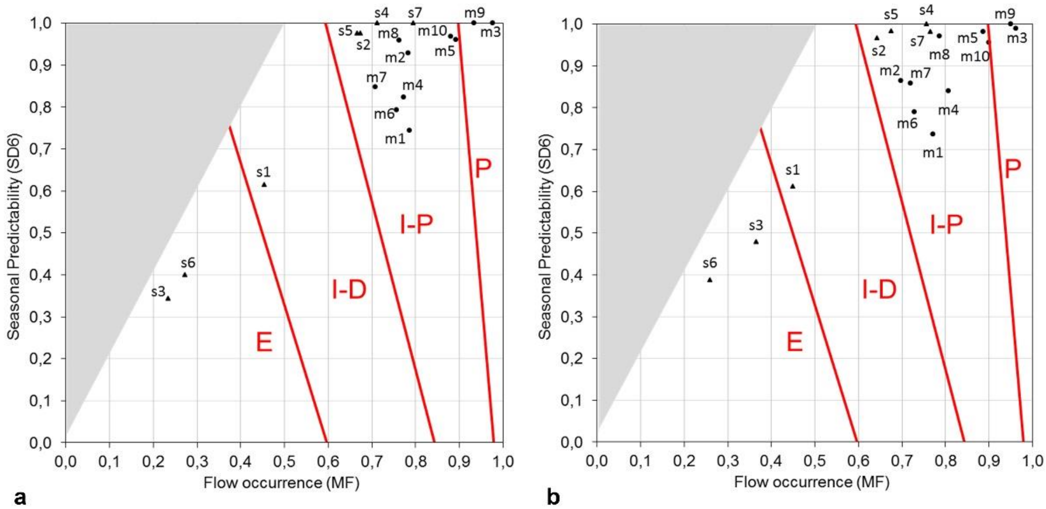

Fig. 9: Stream classification (Gallart et al. 2012) using MF and SD6 derived from flow data (a) and predicted MF and SD6 values based on catchment characteristics (b) (D'Ambrosio et al., 2017a)

5.2 NITROGEN CONCENTRATION IN SURFACE WATERS

In small watersheds in Mediterranean Region most of the sediment and nutrient loads are delivered to the river during floods (De Girolamo et al., 2015a; De Girolamo et al., 2017b; Ribarova et al. 2008). Hence, monitoring flooding is fundamental to estimate annual or seasonal loads. This study was oriented to analyse flood events accurately. For this purpose, a specific program to take samples during floods based on fixed water level changes during rising limb of hydrograph and fixed flow rates during the flood recession was used. Using this sampling strategy during floods, the total number of samples varied between flood events from 3 to 18.

Streamflow and TN concentrations measured from July 2010 to June 2011 at M. Pirro gauging station are shown in Fig. 10.

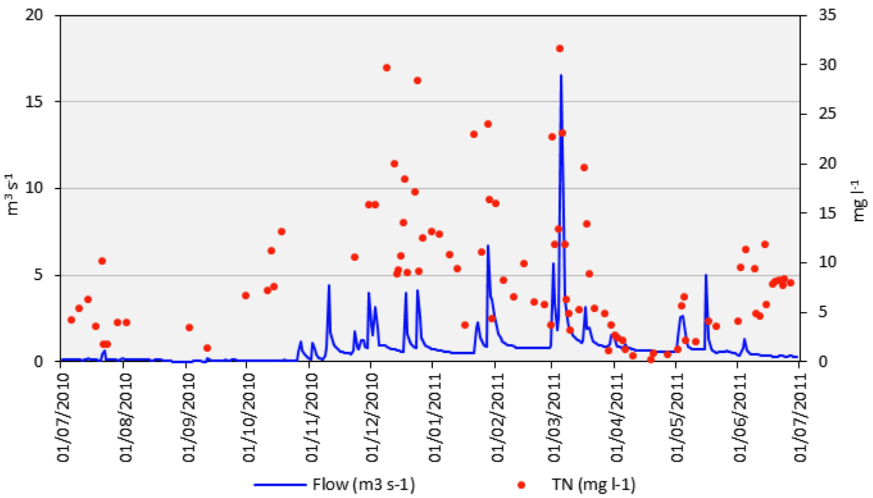

Fig. 10: Hydrograph measured at Masseria Pirro gauging station. TN concentrations are overlapped.

In the hydrograph the wet season (from December to June) and the dry period (from July to November) can be identified. The measured total annual discharge is of 26,052,970 m^3 yr^{-1} (D'Ambrosio et al., 2017b).

The river, at the Masseria Pirro gauging station, shows a very rapid rising stage and a short lag time (time between peak rainfall and peak discharge). Flood duration is typically only a few hours during which N compounds concentrations, as well as streamflow, increase and decrease rapidly. During the study period, dry conditions were recorded only in the secondary reaches while in the main channel a continuous flow was recorded (De Girolamo et al., 2017b).

In the wet season, a wide range of TN concentrations was recorded, while in the dry months the concentrations were included in a more restricted interval. TN concentrations ranged from 0.2 to 31.5 mg l^{-1}. Considering the single N compound, instant measured N-NO_3 concentrations varied between 0.03 and 26 mg l^{-1}, whereas N-NH_4 and TON between 0.01 - 1.67 mg l^{-1} and 0.14 - 33 mg l^{-1} respectively. The highest values were recorded during flood events, especially in autumn and early spring when fertilizers are applied on cereals and olive trees. In most of these events, TON was found to be the predominant component.

In 2010, the D.M. 260/2010 (2010) fixed physico-chemical factors such as dissolved oxygen and nutrients (N-NH_4, N-NO_3, Total P) which are required to support a functioning ecosystem. The Italian Legislative Decree proposed five levels (from high to bad) for these factors and assigned a score to each of these levels introducing the LIMeco index (level of pollution from macro-descriptors related to ecological status). This index is the mean value of the scores assigned to each factor on the measured concentration basis. In this classification, however, supporting elements can only influence High, Good, and Moderate status, while only biological factors can determine Poor or Bad water quality status. If the LIMeco score is poor or bad but the biological indexes are good the ecological status is at least defined moderate. The others parameters, temperature, pH, conductivity and alkalinity, are analysed only to improve the investigations on the biological status. In this study, biological data were not available; hence, here water quality status could not be define. However, the quality standard (Level II - D.M. 260/2010, 2010) for

N-NO_3 (1.2 mg l^{-1}) and N-NH_4 (0.06 mg l^{-1}) are often surpassed. In particular, the highest instant values were recorded during flood events, especially in autumn (26 mg l^{-1} N-NO_3) and early spring (23.4 mg l^{-1} N-NO_3) when fertilizer are mainly applied. Meanwhile during the summer period, in extreme low flow conditions the N-NO_3 concentrations remain over 3 mg l^{-1}.
Fig. 11 shows the Flow Duration Curve (percentage of time during which a specified flow is equaled or exceeded) and N-NO_3 concentrations.

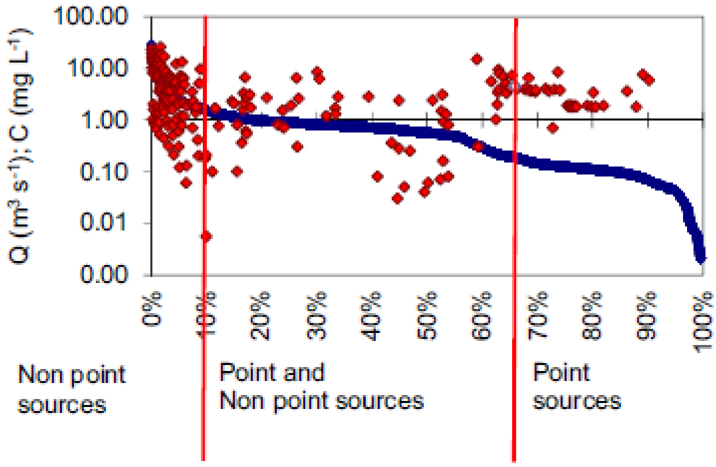

Fig. 11: Flow duration curve and N-NO_3 concentration measurements (De Girolamo et al., 2017b)

In high-flow regime (exc. freq. 0–10%), concentrations decrease in concordance with flow. In contrast, in dry conditions (exc. freq. 65–90%) the concentrations increase to decrease of flow, this behaviour is probably due to a reduction of the dilution effect of the effluent coming from WWTPs. Hence, it can be deducted that point sources are the main causes of pollution in low-flow conditions while non-point source pollution are mainly responsible for high concentrations and loads in high-flow regime (De Girolamo et al., 2017b).
Analysing N-NO_3 concentrations versus streamflow for the entire dataset, the correlation coefficient is 0.59, and the F-test result shows this to be statistically significant (p-value < 0.01). The corresponding coefficient of determination (R^2 = 0.35) indicates that 35% of variance of the concentrations may be explained by streamflow while 65% is justified by other factors such as rainfall intensity and its spatial distribution, vegetation cover, soil and crop management (i.e. tillage, amount and timing of fertilizers), and N input. Meanwhile, the correlation coefficient between TON concentrations and streamflow is 0.47 (p-value < 0.01).
Fig. 12 shows N-NO_3 concentrations versus streamflow.

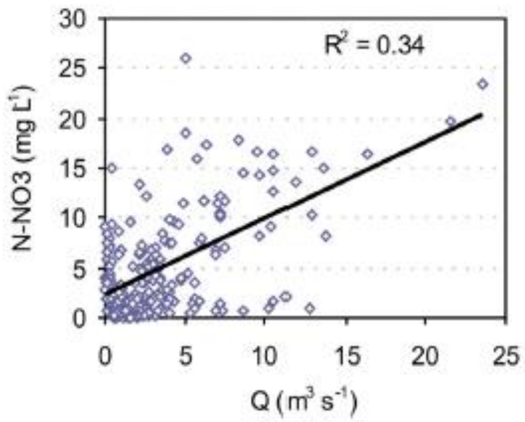

Fig. 12: N-NO3 concentrations versus streamflow measured at Masseria Pirro gauging station (De Girolamo et al., 2017b)

5.3 NITROGEN LOADS IN SURFACE WATERS

The TN annual load, estimated using the four different methods by means of the Loads Tool, ranges between 199,500.4 ($N_{RE,min}$) and 292,336.8 ($N_{RE,max}$) kg yr^{-1} (D'Ambrosio et al., 2017b). The mean value ($N_{RE,mean}$) is 265,853.0 kg yr^{-1} . Thus, as expected, significant differences in the results were found among methods, especially in December, January and March.

Seasonal TN load was characterized by high values in autumn and winter, especially from November to March, when loadings account for 92.3% of the annual load (De Girolamo et al., 2017b). This is mainly due to fertilizers application and rainfall regime. On yearly basis, 36% of TN load is $N\text{-}NO_3$ and 62% corresponds to TON.
Total loads were also evaluated for the most relevant flood events which are represented in the flow duration curve (Fig. 11) in the interval 0–5% of exceedence of frequency. Loads during floods (18 events, 38 days duration) result ∼60% of the annual load, and as a result of several large floods recorded in March, this month account for 26% of annual volume and 35.6% of N load.

5.4 DESCRIPTION OF LOCAL AGRICULTURAL PRACTICES

Table 12 summarises the main agronomic data, provided by interviewed farmers and local dealers, concerning yield, TN fertilizer application rate and irrigation strategies (D'Ambrosio et al., 2017b).

Table 12: Agronomic data. Crops with areas below 100 ha are family-run (D'Ambrosio et al., 2017b)

Crop	Area (ha)	Yield (t/ha)	TN Application Rate (kg/ha)			Irrigated area (ha)	Total annual irrigation (m^3/ha)
			Synthetic fertilizer	Manure	Total		
Durum wheat	2322.5	3.5	129.0	0.0	129.0	0.0	0.0

Crop	Area (ha)	Yield (t/ha)	TN Application Rate (kg/ha)			Irrigated area (ha)	Total annual irrigation (m^3/ha)
			Synthetic fertilizer	Manure	Total		
Deciduous forest	1219.7		0.0	0.0	0.0	0.0	0.0
Olive grove	541.2	2.8	116.0	0.0	116.0	112.5	1500.0
Vetch	478.7	30.0*	80.0	0.0	80.0	0.0	0.0
Sunflower	449.0	3.0	87.0	13.0	100.0	0.0	0.0
Pasture	356.2		0.0	52.9	52.9	0.0	0.0
Winter wheat	312.0	3.1	129.0	0.0	129.0	0.0	0.0
Field bean	249.1	25.0*	0.0	50.0	50.0	0.0	0.0
Bushes and shrubs	234.1		0.0	0.0	0.0	0.0	0.0
Urbanized area	184.2		0.0	0.0	0.0	0.0	0.0
Set-aside land	174.0		0.0	175.0	175.0	0.0	0.0
Deciduous and coniferous forest	168.7		0.0	0.0	0.0	0.0	0.0
Herbage (multiannual)	119.1	21.0*	0.0	49.0	49.0	0.0	0.0
Herbage	94.1	35.0*	0.0	112.0	112.0	38.3	1250.0
Legumes	90.1	2.5	0.0	0.0	0.0	0.0	0.0
Orchard	63.1	16.0	0.0	35.0	35.0	0.0	0.0
Coniferous forest	54.7		0.0	0.0	0.0	0.0	0.0
Vegetable crop	43.0	27.7	120.0	0.0	120.0	43.0	2000.0
Tomato	20.1	78.7	140.0	70.0	210.0	20.1	4500.0
Vineyard	7.8	10.5	90.0	0.0	90.0	7.4	2000.0
Sugar beet	4.1	74.0	80.0	80.0	160.0	0.4	1000.0
Crucifers	3.0	2.5	0.0	80.0	80.0	0.0	0.0
Potato	3.0	15.0	80.0	0.0	80.0	0.0	0.0
Orchard and vegetable crop	2.5	43.7	130.0	0.0	130.0	2.1	2000.0

* Forage yields

Durum wheat is the main crop cultivated in the study area. According to the interviewed farmers, it is mainly fertilised in November and March. The average annual AR throughout the watershed is estimated at 77.7 kg ha^{-1}, although large differences can be found for different crops and management systems (D'Ambrosio et al., 2017b).

Manure produced by animals that are free to roam is directly applied to pasture. Conversely, manure produced by indoor farming is spread on tomatoes, sugar beet, crucifers, herbage, and on crops in rotation with durum wheat (vetch, field bean, sunflower and set-aside land), after a 90-day storage period, aimed at reducing bacterial load. According to the Decree of the Ministry of Agriculture and Forestry (D.M. 7 aprile 2006, 2006), the spreading of manure is not allowed from November to February.
Concerning the irrigation supply, it is provided only during the dry season (i.e., between May and September) to herbage (corn), vegetable, olive grove, tomato, sugar beet and vineyard crops, located near the river in the Troia municipality (Fig. 6). Drip irrigation systems are supplied by surface water withdrawals; no groundwater pumping wells are present, due to the geological structure of the catchment.

As stated by local dealers, the agricultural products are mainly used locally, or sold to Italian companies devoted to food processing; they are rarely exported to foreign countries. On average, 98% of the olive production is used for oil production, and the remaining part is used for the production of table olives and derivatives; the entire vineyard yield goes to wine production.

5.5 NITROGEN BALANCE

The N balance is evaluated for a year at basin scale as a difference between input and output (De Girolamo et al., 2017a). Table 13 summarizes input and output for the whole basin and for hectare of total lands (7200 ha).

Table 13: Nitrogen balance in the Celone catchment computed for a year (July 2010-June 2011)

	N ($kg\ yr^{-1}$)	**N[a] ($kg\ ha^{-1}\ yr^{-1}$)**	**%**
Input			
Synthetic Fertilization (N_{SF})	489977	68.1	72
Animal Farming (N_{AF})	87837	12.2	13
Biological Fixation (N_{BF})	64891	9.0	9
Atmospheric deposition (N_{AD})	39744	5.5	6
Σ Input (Diffuse Sources, DS)	682449	94.8	
Output			
Crop Uptake (N_{CU})	269273	37.4	72
NH_3 volatilization (N_V)	48998	6.8	13
Denitrification in soil (N_D)	57781	8.0	15
Σ Output	376052	52.2	
Σ Input(DS) - Σ Output	306397	42.6	
Riverine export ($N_{RE,mean}$)	265853		
N naturally present in the river (N_{NAT})	10421		
Wastewater sludge (N_{PS})	7050	-	
Riverine export from diffuse sources[b]	248382	34.5	
N in soils and leaching[c]	58015	8.1	

[a] The calculation are referred to total surface area (7200 ha).
[b] It is evaluated subtracting N_{PS} and N_{NAT} to $N_{RE,mean}$
[c] It is evaluated subtracting the Riverine export from diffuse sources to (Σ Input (DS)- Σ Output)

Total input to the catchment from diffuse sources is estimated in about 682.5 t yr^{-1}, corresponding to 94.8 kg ha^{-1} yr^{-1} for whole catchment area, and 134.8 kg ha^{-1} yr^{-1} for productive lands (5065 ha). Fertilizers are the main source of N input (72%), while the animal farming is the second source (13%).

Total output is estimated in 376.1 t yr^{-1}, corresponding to 52.2 kg ha^{-1} yr^{-1} for whole catchment area, and 74.2 kg ha^{-1} yr^{-1} for productive lands.

The surplus, calculated as difference between N input and N output, is 306.4 t yr^{-1}, corresponding to 42.6 kg ha^{-1} yr^{-1} for whole catchment area and about 60 kg ha^{-1} yr^{-1} for productive lands. Riverine export (from diffuse sources) accounts for the main part of this amount (34.5 kg ha^{-1}

yr^{-1} for the whole catchment area), while 8.1 kg ha^{-1} yr^{-1} remains in soil and/or leaches out of soil.

5.5.1 NITROGEN INPUT

5.5.1.1 Nitrogen from fertilizer application

Nitrogen from fertilizers (N_{SF}) was estimated on annual basis by multiplying the AR for the crop area (Table 12). Then, N_{SF} in the catchment boundaries is estimated in 489977 kg ha^{-1} yr^{-}1. In the calculations N from urea and ammonium nitrate was assumed to be lost for volatilization for 10% (Ventura et al., 2008).

Cereals, which are fertilized in November and in March, are the main crops in the study area (2635 ha), and presumably the main source of N. Considering the agricultural lands (4976 ha), TN resulted in 98.5 kg ha^{-1}, while considering the whole watershed area TN was 68.1 kg ha^{-1}.

5.5.1.2 Nitrogen from animal farming

For the study period, nitrogen input from animal farming (N_{AF}) in the catchment boundaries is estimated in 87837 kg ha^{-1} yr^{-1}, corresponding to about 12.2 kg ha^{-1} yr^{-1} for the whole watershed area (De Girolamo et al., 2017b). The number of animals in the catchment, and the N production in fresh manure and after storage and handling for each animal type, both indoor and outdoor farming, is summarized in Table 14. In these calculations, it was assumed that 27.5% of N was lost after manure storage and handling (Fulhage and Pfost, 2002). The losses are not applied to livestock animal.

Table 14: Numbers of animals, animal N production in fresh manure and after storage and handling, total N production on yearly basis. (De Girolamo et al., 2017a)

Beef Cattle	Dairy Cattle	Horse	Sheep Goat	Swine	Poultry	Hen	Rabbit
Number of animals							
313	245	26	2762	816	240200	1276	89
TN production in manure (livestock animal) (kg yr^{-1})							
0	2575	646	13672	1459	13	472	21
TN production in manure (indoor farming) (kg yr^{-1})							
20335	8317	0	0	6339	60038	115	0
TN lost after manure storage and handling (indoor farming) (kg yr^{-1})							
5592	2287	0	0	1743	16510	32	0
Total N production (kg yr^{-1})							
14743	8605	646	13672	6055	43541	555	21

5.5.1.3 Nitrogen from atmospheric deposition

Nitrogen from the atmospheric deposition in the Celone catchment constitutes a minor contribution (De Girolamo et al., 2017b). In fact, based on the recorded average concentration of $N\text{-}NO_3$ (0.33 mg l^{-1}), $N\text{-}NH_4$ (0.237 mg l^{-1}) and TN (0.732 mg l^{-1}), about 5.5 kg TN ha^{-1} yr^{-1} was estimated. The gauging station (PUG1) of the CONEFOR network (LIFE + Futmon Project), where the measurements were made, is located in Apulia Region in the Forestra Umbra (Balestrini and Tagliaferri, 2001). The characteristics of this area are more or less the same of the

Celone basin in terms of economic activities and climate; however, slight differences in terms of loads could be found in the Celone watershed.

Table 15: Atmospheric depositions (N_{AD}) and rainfall recorded at the gauging station Foresta Umbra (PUG1) De Girolamo et al., 2017a

Year	Rain (mm)	$N\text{-}NO_3$	$N\text{-}NH_4$ (kg ha^{-1} yr^{-1})	TON	TN
2010	1209	2.73	1.66	1.34	5.73
2011	1114	2.19	1.55	1.75	5.49
July 2010 - June 2011	1326	2.51	1.79	1.22	5.52

5.5.2 NITROGEN INPUT FROM POINT SOURCES

As mentioned in 3.2 paragraph, three sampling campaigns were performed at the outlet of the three WWTPs. As result, a great variability was found in nutrient concentrations. Based on those data, TN daily loads discharged into the river was estimated in 19.3 kg d^{-1}, which corresponds to an average coefficient of about 7 g d^{-1} EI^{-1} for the sampled months that was extended to the entire period. An annual TN load of 7050 kg/yr (N_{PS}) was then associated to the three WWTPs. Thus, point sources contribution to TN input in the Celone watershed is negligible (about 1% of N) in terms of annual load.

5.5.3 NITROGEN OUTPUTS

Crop uptake, volatilization and denitrification in soils constitute the N output terms (De Girolamo et al., 2017a).

The crop uptake is estimated at about 269 ton yr^{-1}. Table 16 shows surface area for each crop, N crop uptake coefficient used in our calculations, production per hectare and N crop uptake. The N use efficiency of the study agro-ecosystems, defined as the portion of total N inputs removed by the harvest of aboveground part of crops, is 47%, which is in the range of 40–64% found by Brentrup and Palliere (2009) in Europe.

Table 16: N uptake coefficients, crop yields, N crop uptake.

Crop	Surface (ha)	N uptake coefficient	Yield (t ha^{-1})	TN Crop uptake (kg yr^{-1})
Durum wheat	2322.5	22.8	3.5	185922.6
Olive grove	541.2	10.2	2.8	15335.7
Sunflower	449.0	28.0	3.0	37716.0
Winter wheat	312.0	20.3	3.1	19333.7
Orchard	63.1	1.0	16.0	1010.5
Vegetable crop	43.0	4.3	27.7	5123.4
Tomato	20.1	2.6	78.7	4108.0
Vineyard	7.8	2.0	10.5	163.5
Sugar beet	4.1	1.1	74.0	331.3
Crucifers	3.0	14.9	2.5	111.8
Potato	3.0	1.4	15.0	63.0
Orchard and vegetable crop	2.5	-	-	53.1
Total				*269272.6*

Denitrification in soil and the volatilization from urea and ammonium nitrate are estimated in about 58 ton yr^{-1} and about 49 ton yr^{-1}, respectively.

5.6 WATER FOOTPRINT ASSESSMENT

The green (CWU_{green}), blue (CWU_{blue}), grey (CWU_{grey}) and total (CWU_{tot}) water use of crop production per LUS are shown in Fig. 13 and summarised in Table 17 for each crop. For each land use, the table reports the mean (weighted average of LUS values), minimum and maximum values evaluated in the LUSs (D'Ambrosio et al., 2017b). In addition, the crop water use estimated was also reported, using literature values instead of measured ones (CWU_{grey}^{C}), in order to show the discrepancies between values. It was generally found that maximum CWU_{grey} and CWU_{grey}^{C} differ by about one order of magnitude, making evident the diversity of temporary river systems from perennial rivers, and the necessity of measurements. The CWU values changed for the same crop, depending on the type of soil and on the location of the field in the watershed (Table 17).

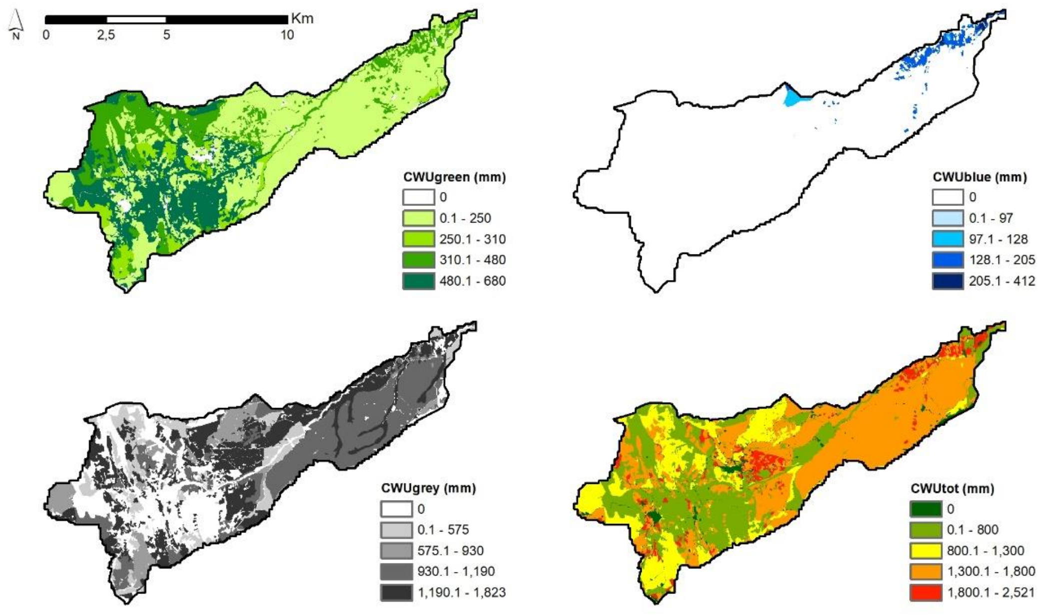

Fig. 13: Green (CWU_{green}) and blue (CWU_{blue}) water use and dilution water requirement (CWU_{grey}) in the study area. CWU_{tot} is obtained summing CWU_{green}, CWU_{blue} and CWU_{grey}. The CWU_{grey} is obtained considering: i) $N_{RE,mean}$ in equations (22) and (23) for α estimation; ii) C_{max} equal to 3 mg l^{-1}; and iii) C_{nat} equal to 0.4 mg l^{-1} (D'Ambrosio et al., 2017b)

Table 17: Crop water use in agricultural production. Minimum (min) and maximum (max) values of LUS are reported. The mean values (mean) are evaluated as the weighted average of the respective LUS values. The CWU_{grey} is obtained considering: i) $N_{RE,mean}$ in equations (22) and (23) for α estimation; ii) C_{max} equal to 3 mg l^{-1}; and iii) C_{nat} equal to 0.4 mg l^{-1}. The CWU_{grey}^{C} is obtained considering: i) α equal to 10%; ii) C_{max} equal to 10 mg l^{-1}; and iii) C_{nat} equal to 0 mg l^{-1} (D'Ambrosio et al., 2017b)

Crop	CWU_{green} (mm)			CWU_{blue} (mm)			CWU_{grey} (mm)			CWU_{grey}^{C} (mm)
	mean	min	max	mean	min	max	mean	min	max	
Bushes and shrubs	498.2	414.4	527.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Coniferous forest	579.5	512.0	679.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Crucifers	222.4	222.4	222.4	0.0	0.0	0.0	781.7	781.7	781.7	80.0
Deciduous and coniferous forest	578.2	537.2	587.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Deciduous forest	509.4	414.6	527.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Durum wheat	235.0	230.4	238.1	0.0	0.0	0.0	1173.7	1071.8	1306.9	129.0
Field bean	218.1	160.8	242.1	0.0	0.0	0.0	550.9	470.5	561.6	50.0
Herbage	212.4	202.4	227.7	46.2	0.0	113.3	1068.9	890.2	1094.3	112.0
Herbage (multiannual)	199.4	174.4	255.9	0.0	0.0	0.0	451.5	389.5	478.8	49.0
Legumes	216.9	176.7	244.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Olive grove	496.9	448.9	552.2	28.9	0.0	139.1	1259.8	1089.1	1300.5	116.0
Orchard	496.5	414.0	525.8	0.0	0.0	0.0	310.4	252.2	316.0	35.0
Orchard and vegetable crop	454.1	431.3	569.7	171.6	0.0	205.3	1268.8	1268.8	1268.8	130.0
Pasture	472.2	471.7	479.7	0.0	0.0	0.0	515.5	419.3	515.7	52.9
Potato	163.0	160.5	203.5	0.0	0.0	0.0	760.6	635.9	781.7	80.0
Set-aside land	188.2	187.3	201.1	0.0	0.0	0.0	1568.8	1261.2	1580.0	175.0
Sugar beet	306.4	302.6	310.1	96.6	96.3	96.8	1362.3	1214.2	1505.7	160.0
Sunflower	271.5	229.6	281.8	0.0	0.0	0.0	921.8	758.9	941.1	100.0
Tomato	286.3	286.3	286.3	411.9	411.9	411.9	1822.7	1822.7	1822.7	210.0
Urbanized area	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Vegetable crop	202.0	194.7	203.8	153.9	128.6	159.0	1045.2	866.1	1084.8	120.0
Vetch	227.1	215.8	235.5	0.0	0.0	0.0	898.6	898.6	898.6	80.0
Vineyard	371.5	363.3	421.2	119.4	0.0	128.4	839.6	715.4	879.4	90.0
Winter wheat	439.7	423.7	446.2	0.0	0.0	0.0	1306.9	1306.9	1306.9	129.0

* The CWU_{grey}^{C} values do not change for the same crop since the leaching-runoff fraction α^{C} considered is constant (10%) and does not depend on the type of soil. Thus, there are not mean, min and max values.

The total WF of crop production in the Celone watershed, between July 2010 and June 2011, was about 79.9 million m^3, of which 30.3%, 0.5% and 69.2% ere constituted by WF_{green}, WF_{blue} and WF_{grey}, respectively; however, WF_{grey}, as well as CWU_{grey}, are highly sensitive to the leaching-runoff fractions and to the water standards applied, as described in Section **5.6.3**.

The crop having the highest WF was olive, followed by winter and durum wheat (Fig. 14). Obviously, WF_{blue} and WF_{grey} were not associated with rain-fed crops or non-fertilised crops, respectively. Legumes relied only on green water.

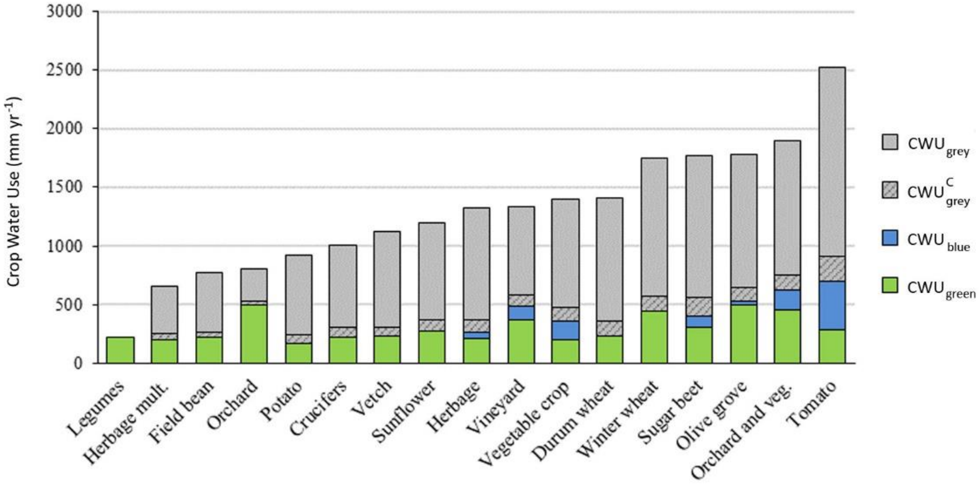

Fig. 14: The WF of crop production in the Celone watershed. The WF_{grey} was obtained considering: i) $N_{RE,mean}$ in equations (22) and (23) for α estimation; ii) C_{max} equal to 3 mg l^{-1}; and iii) C_{nat} equal to 0.4 mg l^{-1}. The WF_{grey}^{C} was obtained considering: i) α equal to 10%; ii) C_{max} equal to 10 mg l^{-1}; and iii) C_{nat} equal to 0 mg l^{-1} (D'Ambrosio et al., 2017b)

The WF_{blue} is generally less than the irrigation volume (I), applied over the growing period as a whole. The difference refers to irrigation water that runs off from the field and/or percolates to the groundwater (Hoekstra et al., 2011).

The only crops that never reached a water stress coefficient (K_s) value below 0.5 during the study periods are durum wheat, pasture, irrigated herbage, tomatoes and vegetables, as well as set-aside land (D'Ambrosio et al., 2017b). In particular, the annual average K_s of durum wheat is always equal to 1 in the whole watershed, even if it is entirely rain-fed. Contrariwise, if there was no irrigation, also herbage, tomatoes and vegetables would have been water-stressed, and the K_s would have been equal to zero in the summer months (June to August).

5.6.1 RUNOFF CALIBRATION

The CWU_{green} evaluation was made by means of the soil-water balance model, based on equation (14) (D'Ambrosio et al., 2017b). Therefore, the surface runoff was preliminarily determined using the calibration procedure described above.

Monthly mean values (m^3 s^{-1}) of the daily streamflow recorded at MP (Q_{MP}), daily mean baseflow (BF) and interflow (IF), as well as the volumes (m^3) of surface runoff (SF_{MP}), estimated through the study period and used in the calibration procedure (equation (19)), are reported in Table 18. The SF_{MP} represents 11.4% of the total annual rainfall.

Table 18: Monthly mean values of daily streamflow recorded (Q_{MP}), and daily mean baseflow, interflow (BF+IF) and surface runoff (SF_{MP}) (D'Ambrosio et al., 2017b)

Month	Q_{MP} ($m^3 s^{-1}$)	BF+IF ($m^3 s^{-1}$)	SF_{MP} ($m^3 s^{-1}$)	SF_{MP} (m^3)
Jul 10	0.16	0.11	0.03	92839.8
Aug 10	0.09	0.08	0.00	2305.8
Sep 10	0.08	0.04	0.02	58699.0
Oct 10	0.17	0.08	0.08	204177.1
Nov 10	0.98	0.48	0.48	1238397.3
Dec 10	1.32	0.89	0.43	1140998.2
Jan 11	1.20	0.70	0.49	1313658.7
Feb 11	1.30	0.93	0.36	867329.0
Mar 11	2.46	1.49	0.96	2571332.5
Apr 11	0.71	0.70	0.01	14243.3
May 11	1.04	0.70	0.33	872074.0
Jun 11	0.42	0.36	0.05	134027.7

Calibrated curve numbers (CN II) show a very high variability that depends on the antecedent moisture condition (AMC) of the rainfall zones, but also on the runoff coefficient (C). Generally, when the 10-day period was characterised by a C value higher than 25% and AMC I, it was not possible to assign different CN values to the 103 identified LUSs, in order to equalise SF_{MP}. Therefore, a constant high value throughout the watershed was assigned. Table 19 shows the monthly mean CN II obtained, following the calibration procedure.

Generally, calibrated CNII values are highly variable in the same LUSs throughout the study period, and are higher than those given in the tables of the USDA (1986) (D'Ambrosio et al., 2017b).

Table 19 Monthly mean runoff coefficient (C) and calibrated curve numbers (CNII). Minimum (Min) and maximum (Max) values for 10-day time periods are also reported (D'Ambrosio et al., 2017b)

	Jul 10	Aug 10	Sep 10	Oct 10	Nov 10	Dec 10	Jan 11	Feb 11	Mar 11	Apr 11	May 11	Jun 11	Min	Max
C (%)	1.3%	4.4%	1.1%	2.2%	10.9%	18.7%	22.6%	19.7%	26.6%	0.2%	17.7%	4.0%	0%	57.4%
Crop and soil group	**Calibrated Curve Numbers (CN II)**													
Durum wheat C	70.66	74.00	85.88	75.30	87.67	82.85	75.09	80.98	78.65	70.55	89.23	87.30	44.64	99.63
Durum wheat D	72.66	81.00	87.88	78.96	92.33	89.85	82.09	83.31	85.65	77.55	93.90	90.96	51.64	99.63
Forest, bushes and shrubs C	61.66	77.00	76.88	70.30	89.67	85.85	78.09	81.98	81.65	73.55	91.23	82.30	41.91	99.63
Forest, bushes and shrubs D	67.66	83.00	82.88	76.30	93.67	91.85	84.09	83.98	87.65	79.55	95.23	88.30	47.91	99.63
Herbage C	70.66	77.00	85.88	76.30	95.67	94.85	81.09	84.98	90.65	79.55	91.23	82.30	81.90	98.84
Herbage D	72.66	82.00	87.88	79.30	97.00	96.85	85.09	85.64	92.65	82.55	94.56	87.30	86.90	98.84
Herbage multiannual C	70.66	77.00	85.88	76.30	95.67	94.85	81.09	84.98	81.65	73.55	91.23	82.30	60.20	98.84
Herbage multiannual D	72.66	82.00	87.88	79.30	97.00	96.85	85.09	85.64	86.65	78.55	94.56	87.30	65.20	98.84
Legumes C	70.66	81.00	85.88	77.63	95.67	94.85	83.75	84.98	85.65	77.55	93.90	87.96	64.20	98.84
Legumes D	72.66	86.00	87.88	80.63	97.00	96.85	87.75	85.64	90.65	82.55	97.23	91.96	69.20	98.84
Potato C	70.66	81.00	85.88	77.63	95.67	94.85	83.75	83.31	85.65	77.55	93.90	89.63	51.64	99.60
Potato D	72.66	84.00	87.88	79.96	97.00	96.85	86.42	84.31	88.65	80.55	95.90	91.96	54.64	99.60
Crucifers D	72.66	84.00	87.88	79.96	97.00	96.85	86.42	85.64	89.99	83.22	98.56	91.96	83.31	98.68
Sugar beet C	70.66	77.00	85.88	76.30	89.67	85.85	78.09	81.98	81.65	73.55	91.23	82.30	47.64	99.63
Sugar beet D	72.66	81.00	87.88	78.96	92.33	89.85	82.09	83.31	85.65	77.55	93.90	86.30	51.64	99.63
Winter wheat C	70.66	77.00	85.88	76.30	89.67	85.85	78.09	81.98	81.65	73.55	91.23	82.30	47.64	99.63
Winter wheat D	72.66	81.00	87.88	78.96	92.33	89.85	82.09	83.31	85.65	77.55	93.90	86.30	51.64	99.63
Set-aside land C	70.66	86.00	85.88	79.30	95.67	94.85	87.09	84.98	90.65	82.55	97.23	91.30	50.91	99.63
Set-aside land D	72.66	88.00	87.88	81.30	97.00	96.85	89.09	85.64	92.65	84.55	98.56	93.30	52.91	99.63
Sunflower C	68.66	84.00	85.88	78.63	95.67	94.85	85.75	84.98	90.65	81.22	95.90	89.30	48.91	98.84
Sunflower D	70.66	86.00	87.88	80.63	97.00	96.85	87.75	85.64	92.65	83.22	97.23	91.30	50.91	98.84
Tomato C	68.66	84.00	85.88	78.63	95.67	94.85	85.75	84.98	90.65	81.22	95.90	89.30	48.91	98.84

	Jul 10	Aug 10	Sep 10	Oct 10	Nov 10	Dec 10	Jan 11	Feb 11	Mar 11	Apr 11	May 11	Jun 11	Min	Max
C (%)	1.3%	4.4%	1.1%	2.2%	10.9%	18.7%	22.6%	19.7%	26.6%	0.2%	17.7%	4.0%	0%	57.4%
Tomato D	70.66	86.00	87.88	80.63	97.00	96.85	87.75	85.64	92.65	83.22	97.23	91.30	50.91	98.84
Olive and orchard C	65.66	81.00	80.88	74.30	92.33	89.85	82.09	83.31	85.65	77.55	93.90	86.30	45.91	99.63
Olive and orchard D	68.66	84.00	83.88	77.30	94.33	92.85	85.09	84.31	88.65	80.55	95.90	89.30	48.91	99.63
Urbanized area C	71.66	87.00	86.88	80.30	96.33	95.85	88.09	85.31	91.65	83.55	97.90	92.30	51.91	99.63
Urbanized area D	73.66	89.00	88.88	82.30	97.67	97.85	90.09	85.98	93.65	85.55	99.23	94.30	53.91	99.99
Vegetable C	69.66	85.00	85.88	78.96	95.67	94.85	86.42	84.98	90.65	81.88	96.56	90.30	49.91	98.84
Vegetable D	72.66	88.00	87.88	81.30	97.00	96.85	89.09	85.64	92.65	84.55	98.56	93.30	52.91	98.99
Vineyard C	64.66	80.00	79.88	73.30	91.67	88.85	81.09	82.98	84.65	76.55	93.23	85.30	44.91	99.63
Vineyard D	70.66	86.00	85.88	79.30	95.67	94.85	87.09	84.98	90.65	82.55	97.23	91.30	50.91	99.63

5.6.2 LEACHING AND RUNOFF FRACTION CALIBRATION

As described in Section 3.6.3, the leaching-runoff fraction was divided between runoff ($\alpha_{R,k}$) and leaching ($\alpha_{L,k}$) by slightly modifying the procedure suggested by Franke et al. (2013) (D'Ambrosio et al., 2017b). Then, the values of $\alpha_{R,k}$ and $\alpha_{L,k}$ associated with each LUS were properly calibrated, by equating equation (25) to equation (27), and equation (26) to equation (28), respectively. Considering $N_{RE,min}$, $N_{RE,mean}$ and $N_{RE,max}$ in equations (27) and (28), R was estimated as 77,394.2, 143,746.8 and 170,230.6 kg yr^{-1}, whereas L was 32,176.5, 0 and 0 kg yr^{-1}, respectively. The values of $\alpha_{R,k}$ and $\alpha_{L,k}$ obtained are properly merged (weighted mean), based on the soil use in Table 20. Thus, α_R and α_L values are shown.

Table 20: Leaching and runoff fraction (α_L, α_R) associated with fertilised crops in the Celone watershed (D'Ambrosio et al., 2017b)

Crop	α_L				α_R			
	Franke et al. (2013)	$N_{RE,min}$	$N_{RE,mean}$	$N_{RE,max}$	Franke et al. (2013)	$N_{RE,min}$	$N_{RE,mean}$	$N_{RE,max}$
Crucifers	0.09	0.05	0.00	0.00	0.14	0.14	0.25	0.30
Durum wheat	0.11	0.06	0.00	0.00	0.13	0.13	0.24	0.28
Field bean	0.11	0.06	0.00	0.00	0.16	0.15	0.29	0.34
Herbage	0.09	0.05	0.00	0.00	0.14	0.13	0.25	0.29
Herbage (multiannual)	0.10	0.05	0.00	0.00	0.14	0.13	0.24	0.28
Olive grove	0.11	0.06	0.00	0.00	0.16	0.15	0.28	0.33
Orchard	0.08	0.04	0.00	0.00	0.13	0.12	0.23	0.27
Orchard and vegetable crop	0.09	0.05	0.00	0.00	0.14	0.14	0.25	0.30
Pasture	0.09	0.05	0.00	0.00	0.14	0.14	0.25	0.30
Potato	0.09	0.05	0.00	0.00	0.14	0.13	0.25	0.29
Set-aside land	0.08	0.04	0.00	0.00	0.13	0.13	0.23	0.28
Sugar beet	0.10	0.05	0.00	0.00	0.12	0.12	0.22	0.26
Sunflower	0.08	0.05	0.00	0.00	0.14	0.13	0.24	0.28
Tomato	0.07	0.04	0.00	0.00	0.13	0.12	0.23	0.27
Vegetable crop	0.08	0.04	0.00	0.00	0.13	0.12	0.23	0.27
Vetch	0.10	0.06	0.00	0.00	0.16	0.16	0.29	0.35
Vineyard	0.09	0.05	0.00	0.00	0.14	0.13	0.24	0.29
Winter wheat	0.09	0.05	0.00	0.00	0.15	0.14	0.26	0.31

The α_R values obtained from the calibration procedure are higher than those obtained by applying the procedure suggested by Franke et al. (2013). Moreover, they are highly variable, depending on the load value (N_{RE}) considered. Leaching occurs only if $N_{RE,min}$ is considered in equation (28), since only in this case was TN in soil and leaching (L) estimated at higher than zero (D'Ambrosio et al., 2017b).

5.6.3 UNCERTAINTY IN GREY WATER FOOTPRINT ASSESSMENT

Although the WF assessment is based on a large set of assumptions, so that the outcomes carry considerable uncertainties, little attention has been paid to their quantification (Hoekstra et al., 2011; Mekonnen and Hoekstra, 2010; Zhuo et al., 2016). Uncertainty may originate from four sources: (i) context (system boundaries); (ii) input data; (iii) parameterisation; and (iv) model (Walker et al., 2003). A first detailed study of the uncertainties in the estimation of WF_{green} and WF_{blue}, associated with input data and parameters (precipitation, reference evapotranspiration, crop coefficient, crop calendar, soil-water content at field capacity, yield) was performed by Zhuo et al. (2014), by means of Monte Carlo simulations. Afterwards, Kersebaum et al. (2016) assessed the uncertainties of WF_{green} and WF_{blue} originating from the use of seven different crop-growth models for crop yield and evapotranspiration estimates. Instead, the WF_{grey} uncertainties, due to primary data (such as plant density, irrigation, fertilisation, harvesting), were quantified by Gil et al. (2017).

In the present study, an attempt to estimate uncertainty associated with the parameters α, C_{max} and C_{nat} values, was made (D'Ambrosio et al., 2017b). In particular, the WF_{grey} was quantified by applying different combinations of α, C_{max} and C_{nat} values:

- calibrated α values ($\alpha_{L,k}$; $\alpha_{R,k}$) – 3 mg l^{-1} to 0.4 mg l^{-1} (CWU_{grey});
- most commonly-used values ($\alpha_{L,k}$; $\alpha_{R,k}$) – 10% –10 mg l^{-1} to 0 mg l^{-1} (CWU_{grey}^{C}).

In the first case, $N_{RE,min}$, $N_{RE,mean}$ and $N_{RE,max}$ were used in equations (27) and (28), for TN runoff (R) and TN in soil and leaching (L) estimates, in order to calibrate $\alpha_{L,k}$ and $\alpha_{R,k}$ values. Hence, three different combinations of ($\alpha_{L,k}$; $\alpha_{R,k}$) were defined for each LUS, as well as different values of CWU_{grey}.

Considering the single crops, LUS CWU_{grey} values were statistically analysed, and a box-plot was built (Fig. 15). As the coefficient of variation was higher than 0.4, mean values and standard deviations were used within the box-plot representation.

Fig. 15 points out the high variability of CWU_{grey}, depending on α-C_{max}-C_{nat} combination. Between crops, tomato shows the highest variability, ranging from 21 (CWU_{grey}^{C}) to 2,220 mm (mean CWU_{grey} value plus standard deviation). Conversely, the CWU_{grey} associated with orchards varies between 35 (CWU_{grey}^{C}) and 374 mm (maximum CWU_{grey} between orchard LUSs), and is the least variable. The variability is directly proportional to the TN application rate.

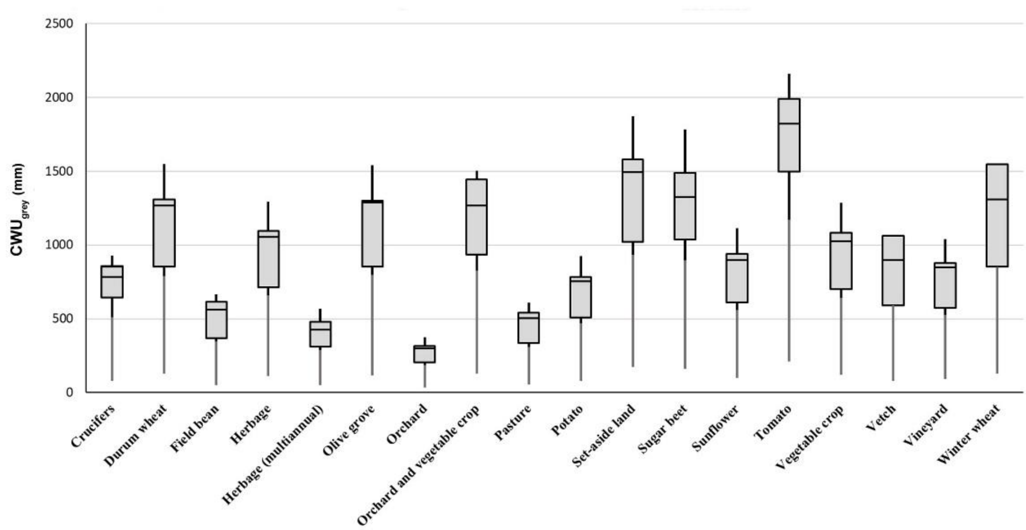

Fig. 15: CWU_{grey} box-plot. The black lines depict CWU_{grey} minimum and maximum values. The grey lines depict CWU_{grey}^{C} values (D'Ambrosio et al., 2017b)

5.7 WATER FOOTPRINT SUSTAINABILITY ASSESSMENT

The average results of the green and blue water sustainability analysis, calculated on a monthly scale from July 2010 to June 2011, are depicted in Fig. 16.

According to our estimate, green water management is sustainable in the river basin, as a whole, since WS_{green} is lower than 1 throughout the study period. Indeed, the WS_{green} ranges between 0.21 (September 2010) and 0.99 (April 2011), with an average annual value equal to 0.72 (D'Ambrosio et al., 2017b).

Conversely, the results obtained from the WS_{blue} index evaluation contrast, depending on the environmental flow requirement value considered. If the threshold of 0.05 m^3 s^{-1} (EFR) is used, as established by the river basin authority, WS_{blue} varies between zero (November 2010 to April 2011, i.e., the period when water withdrawal for irrigation does not occur) to 0.98 (September 2010), and water scarcity is then classified as low. Contrariwise, if it is assumed that EFR accounts for an 80% share of the R_{nat} (EFR^{C}), significant water scarcity is registered during the summer months (from July 2010 to September 2010). Indeed, WS_{blue} ranges from zero to 1.72 (WS_{blue}^{C}).

The average annual WS_{blue} is 0.15 or 0.71, depending on the EFR considered. Hence, blue water management shows sustainability on a yearly time-scale.

Conversely, the analysis of the WPL surface-water values reveals that surface-water pollution in upstream river streams was unsustainable, when WF_{grey} is considered. Indeed WPL is equal to 2.2. Meanwhile, if WF_{grey}^{C} is used, the WPL becomes equal to 0.2, and the assimilative capacity of the Celone River was not fully consumed.

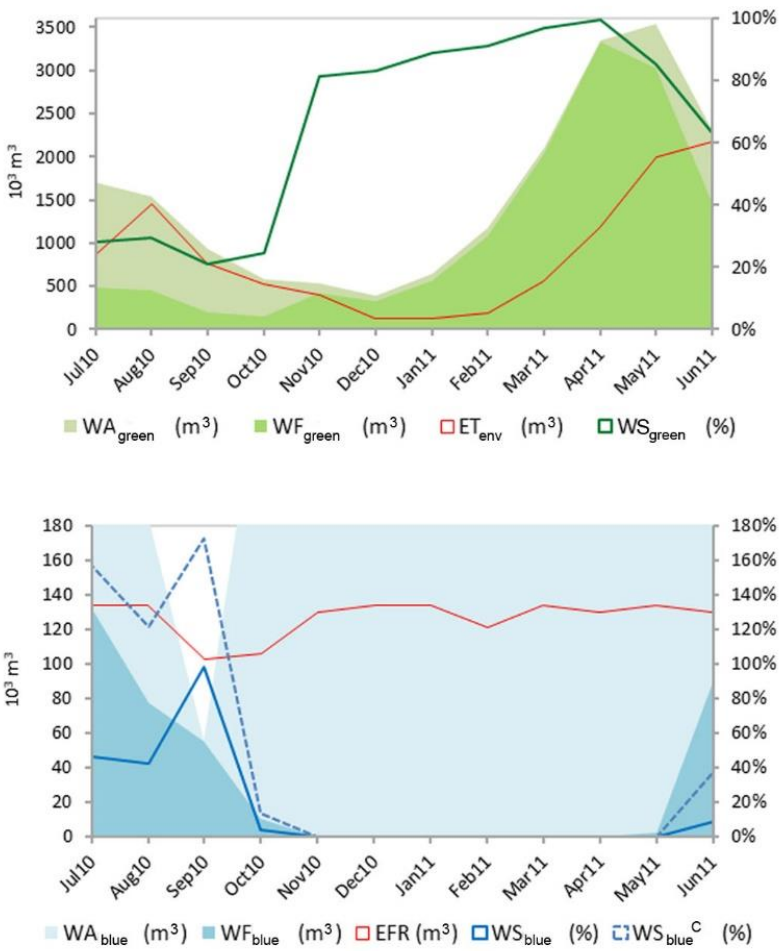

Fig. 16: Monthly green and blue water scarcity indices for the Celone watershed (D'Ambrosio et al., 2017b)

6 DISCUSSION

6.1 HYDROLOGICAL REGIME CHARACTERIZATION

The first case study presented in this work is an attempt to establish a method to support ecologists and water resources managers in the WFD implementation process (D'Ambrosio et al., 2017a). It is applicable to data-scarce regions with temporary river systems. Across the Mediterranean Basin, temporary river systems are common as is the paucity of data, which makes their characterisation and classification more difficult than in perennial river systems. An intermittent flow with a shift between lotic and lentic conditions through the year may influence biotic composition significantly (Buffagni et al., 2009). As a consequence, biological communities may be temporally poorer in diversity and taxa than perennial rivers. Hence, it is easy to understand that the river type classification and the characterisation of the flow regime constitute a precondition to assess the water quality status in these river systems. Due to the peculiarities of temporary river systems, the implementation of the WFD has been delayed indicating the need for specific tools that address the special character of such water bodies (Nikolaidis et al., 2013). Considering the timetable of the WFD, the development of new methods is desirable because of the pending review and update of the second River Basin Management Plan (2021).

In response, the practicality of a methodology based on established techniques and data which is easy to use by technicians and water resources managers, was assessed using a case study. The assessment was completed by:

i. identifying a set of non-redundant HIs able to describe the main characteristics of flow regime in the study area;
ii. linking relevant indicators to catchment characteristics by fitting a regression procedure to define the relationships which can be used to evaluate hydrological indicators in ungauged sites.

A total of ten gauging stations were analysed because a larger dataset of measured data was not available across the entire study region. The need for at least twenty years of daily flow data to characterise flow variability adequately, and to calculate HIs as suggested in the literature (Huh et al., 2005; Konrad and Booth, 2002; Ritcher at al., 1997) is acknowledged as a limiting factor. Despite this limitation, the study provides valuable insight into in the context of temporary river systems (D'Ambrosio et al., 2017a).

Several studies can be found in the literature that have analysed streamflow regime using metrics (Mackay et al., 2014; Poff et al. 2010). Hence, PCA was used to identify the most representative metrics describing specific flow characteristics. HIs were identified which are able to differentiate between hydrological regimes in temporary rivers. It was found that a subset of 13 metrics, including at least one metric from each of the four significant flow characteristic groups (magnitude, duration, frequency and rate of changes), explained most of the variability in flow regime for all gauging stations. Among them, some indicators represent the magnitude of high-flow conditions i.e. January and March mean flow (MAJ; MAMar). Other indicators represented the magnitude of maximum annual flows of 30 and 90-day duration (DH4, DH5) and some represented the variability and predictability (FI_RB, MF and SD6) and the degree of temporariness (number of zero days, DL6). However, it should be noted that the analysis considered streams with a low degree of temporariness.

It is assumed that different HIs can be identified if the PCA is performed with a new dataset which includes a number of ephemeral and intermittent river reaches.

The use of regression models to provide links between indices and sets of catchment descriptors is a long-established practice in hydrology (Murphy et al., 2013). Many studies have identified watershed size and shape, climate, geology, soil type, topography and land cover as features largely determining river flow regime patterns (Baker et al., 2004; Chiverton et al., 2014; Poff et al., 1997; Snelder and Biggs, 2002). Carlisle et al. (2010) found that soil properties, precipitation and topography were the most important predictors of average flow metrics. In this study, it was found that the catchment area, mean annual rainfall, mean watershed slope, gauging station elevation, soil hydraulic conductivity, available water content and the extent of agricultural areas are the most important features influencing river flow regime.

The regression analysis results show that some HIs can be successfully represented by linear models and others by means of second order models, as confirmed by the statistical index, graphical tool and test checks. Hence, it can be said that despite their limitations, regression models allow the estimation of some relevant characteristics of hydrological regime in the absence of measured data. However, knowledge of the hydrological processes, study area characteristics and anthropogenic impacts are necessary for applying a regression model (D’Ambrosio et al., 2017a).

A stream classification using MF and SD6 derived from measured flow data and predicted MF and SD6 values based on catchment characteristics by means of the best regression model (second order polynomial) was tested in this study. In the United States, MF is a widely used metric for the identification of intermittent streams (Poff, 1996). In the wet-dry tropical region of Australia, Moliere et al. (2009) developed a stream classification technique based on flow variability indices. Oueslati et al. (2015) used predictability, zero flow days and the FI_RB for classifying Mediterranean rivers. Depending on the aim of the classification, different methods and metrics can be selected. In this study, to differentiate between flow statuses relevant for biota, a classification was used designed specifically for temporary river systems tested in river basins across the Mediterranean (Gallart et al., 2012; Tzoraki et al., 2015).

The classification of the stations using catchment characteristics was found to be the same as the station classifications based on long-term flow data.

In summary, there are a number of limitations in this study that could be further explored to refine the technique of using catchment characteristics to estimate the flow regime of a stream. The limitations include:

i. the limited number of gauging stations;
ii. the flow data quality (hydrological indices were derived for each station irrespective of the quality of the flow data collected at the site);
iii. the catchment characteristics (catchment characteristics analysed in this study were limited and it may be possible to identify alternative parameters that may be more appropriately used to enhance the significance of the indices regression equations i.e. lithology and geology).

The results of this study demonstrate that an increase of the number of the gauging stations, simulated by using streamflow data, might better address the error introduced by performing the analysis on a limited number of sites.

Despite these limitations, it is considered that the outcomes of this study can provide valid support to river basin managers (D’Ambrosio et al., 2017a). The potential to estimate the metrics in ungauged sites without using complex hydrological models, which generally require large datasets and skilled operators, provides a vital tool for watershed management. The hydrological indicators are an efficient tool to summarise and represent specific aspects of a riverine system. For instance, high flow components (MAJ, MAMar, DH4 and DH5) provide information on the water availability, while FI_RB indicates the response to rainfall events which can be used to inform flood management. Furthermore, the analysis shows that predicted hydrological indices can be used to classify hydrological regimes of ungauged rivers in accordance with the WFD, as long as attention is paid to anthropogenically altered river networks.

6.2 NITROGEN CONCENTRATIONS AND LOADS IN SURFACE WATER

The Celone stream has a flow regime characterized by typical semi-arid features with a seasonal pattern of a drought period and flash floods (De Girolamo et al., 2017b). The hydrograph shows a very rapid rising stage and a short lag time (time between peak rainfall and peak discharge). Flood duration is typically only a few hours during which N concentrations, as well as streamflow, increase and decrease rapidly. These peculiarities of the flow regime suggest that specific monitoring activities are needed, which accurately analyse peak discharge in addition to the normal- and low-flow conditions to estimate annual or seasonal loading of nutrients.

Discrete concentration data are useful for comparison to existing water quality standards but they are not sufficient to assess pollutant loads over a long period (e.g. month, season, year). For this reason, a ‘‘flood oriented’’ strategy to obtain an acceptable load estimation was defined.

The temporal dynamic of N transport in the Celone catchment showed a high variability: intra-annual, monthly and within-event. Indeed, regarding N-NO_3, the median value of concentrations in normal-flow conditions was found 3.8 mg l^{-1}. However, samples covering all the flow conditions show a wide range of N-NO_3 concentrations with the highest values recorded during flood events (26 mg l^{-1}). Generally, after the high-flow or multiple events the N-NO_3 concentrations was found below 1 mg l^{-1}, while, during the summer period, in extreme low-flow conditions the concentrations remain always over 3 mg l^{-1}. Meanwhile throughout the study period TN concentrations ranged from 0.2 to 31.5 mg l^{-1}.

Similar concentration values may produce different effects whose quantification needs additional studies and analysis. In fact, eutrophication is the result of nutrient enrichment in the water bodies, but the severity of the phenomenon depends on the specific watershed characteristics, climate, morphology, water residence time, nutrient concentration and ratio, and generally on the ecosystem resilience. Camargo and Alonso (2006) performed an extensive study on the ecological and toxicological effects of inorganic N pollution in aquatic ecosystems and found that TN levels lower than 0.5–1.0 mg l^{-1} might prevent aquatic ecosystems from developing eutrophication and acidification floods (De Girolamo et al., 2017b).

N load is mainly transported in winter and spring, when floods with high magnitude occurred, vegetation cover is absent or very low and tillage operations and fertilizers application are generally performed. The highest losses of N in the efflux water were recorded in March, as consequence of several extremely high rainfall events. However, part of N load in this period surely derived from fertilizers, which were supplied to cereals (durum wheat and winter wheat). At yearly basis, it was estimated a TN exportation from the basin to the river of about 36.9 kg ha^{-1} yr^{-1}. This value is higher than estimated annual export rates of nutrient in similar basins located in the South of Italy (De

Girolamo et al., 2012a), but it is in the range of 26–50 kg ha^{-1} yr^{-1} estimated by Bouraoui et al. (2009) for the study area for the year 2000.
Similar studies carried out in Europe reported a wide range of N losses, from 1.5–19 kg ha^{-1} yr^{-1} for extensive agricultural watershed (Parn et al., 2012) to more than 100 kg ha^{-1} yr^{-1} for intensive agricultural watershed (Hatfield and Follett, 2008). However, it should be pointed out that quantification of the nutrient loads is strongly influenced by both the sampling frequency and the load estimation algorithm used for the calculation (Williams et al., 2015). As demonstrated in the current study, depending on the sampling strategy and on the approach used for the calculations, a very large interval of variation in N flux can be found floods (De Girolamo et al., 2017b).
Moreover, several studies reported losses with a large variation among years (Ventura et al., 2008) depending mainly by the hydrological regime. As mentioned above (Table 6), the study period can be classified as a wet year. In fact, rainfall measured from July 2010 to June 2011 was 1193.4 mm (Faeto gauge), it was 45% higher than the average value recorded from 1950 to 2012 (822.3 mm).
Hence, it is expected that in dry period N losses are sensibly lower than that calculated here. Indeed, it is well known that riverine N loads tend to be substantially higher during wet years (high annual precipitation, or extreme rainfall events), because of increased erosion and transport of the nutrients to stream channels.
Based on the present study, it is possible to say that the high level of N efflux in surface water predict a surplus of N in the river basin, as demonstrated with the performed N balance.
N excess may have a great impact on the health of the river and the downstream reservoir. More efficient fertilizers and management practices are needed to reduce N input.

6.3 NITROGEN BALANCE

In the present study, the N balance in the Celone watershed was assessed. This watershed is representative of a larger area including the Monti Dauni where all the tributaries of the Candelaro river have their origin and for this reason data collected here are important for the management of the whole Candelaro river basin.
The N budget at catchment scale in the study period shows a surplus. As expected in the Celone catchment, as for the majority of European catchment, N input is mainly related to the antropoghenic pressures (European Environment Agency, 2005). The major anthropogenic source of nitrogen is represented by the chemical fertilizers. Animal farming is also an important contribution, while point sources constitute a negligible contribution in terms of annual loads but it is relevant in terms of concentrations in extreme low-flow conditions. Total N input from anthropogenic activities (synthetic fertilizers, animal farming and wastewater sludge) was estimated in about 81.3 kg ha^{-1} yr^{-1} for the whole watershed area (7200 ha). Most of the N left the area by crop yields and by riverine export.
The surplus at the catchment level, defined as the difference between N input and output, was estimated in about 43 kg ha^{-1} yr^{-1} of total area and about 60 kg ha^{-1} yr^{-1} for productive lands floods (De Girolamo et al., 2017a).
Literature data report a wide variability of yearly N balance due to the different characteristics and agricultural peculiarities of the studied basins and to the various approaches used for calculating the nutrient balance (Pieri et al., 2011). Leip et al. (2011) in their study found N surplus for EU Member States between 55 kg N ha^{-1}yr^{-1}and more than 200 kg N ha^{-1}yr^{-1}for the soil N-budget. The higher

values were found for countries with a high animal density, which is calculated to be up to 3.6 and 4.6 live-stock units per hectare of agricultural area in the Nether lands and Malta, respectively. N surplus results generally low in countries specialized in extensive crop production, such as Bulgaria (23 kg N $ha^{-1}yr^{-1}$) and Romania (15 kg N $ha^{-1}yr^{-1}$). In Italy, in a heavily impacted watershed of the Po Plain (Northern Italy), Bartoli et al. (2012) found an elevated surplus averaging 180 kg $ha^{-1}yr^{-1}$ for arable land, while Ventura et al. (2008) in an agricultural deltaic territory of the Po valley presented a negative balance (−7.6 kg ha^{-1}), and Isidoro et al. (2006) in Spain estimated N surplus in 68 kg ha^{-1}. These results suggest that a particular caution have to be used when using literature data. In the Celone catchment, the N surplus is only partially compensated at basin level by the riverine export (De Girolamo et al., 2017a). The remaining amount, mainly in the form of nitrate, probably percolates through unsaturated soil towards groundwater. In part it is retained in soils in different N forms, and in part is metabolized in the catchment or in the river network. Although further analysis is needed to understand the capacity of the catchment to metabolize a fraction of the surplus, and supplementary studies are needed to understand the impact of WWTPs effluents on river ecosystems.

6.3.1 UNCERTAINTY IN NUTRIENT BALANCE CALCULATIONS

A considerable uncertainty can affect the computation of the N balance at basin scale (De Girolamo et al., 2017a). Possible causes of biases and errors can be found in the data, samplings methodology, measurements, data manipulations, and estimations (Oenema et al., 2003).
The Celone catchment is characterized by a high spatial variability of rainfall and by a very fractioned land use, where dissimilar amounts and types of fertilizers are used in the upper and lower part of the basin. For this reason, official data usually available at regional or provincial level were not representative for the study area (i.e., crop yields and fertilizer amounts). Hence, a generalization in upscaling and downscaling of information and data may cause errors in nutrient budget. There is an inevitable personal interpretation of the data and of the agro system, which can bring to a different schematization and to dissimilar results in N budget. Lack of data and knowledge concerning the biological fixation, volatilization and denitrification makes it difficult to estimate a true value of these factors. In this work, the estimation was based on some literature data when information from the study area was not available. Anyway, those values can be affected by a large uncertainty. On the other hand, the actual denitrification under field conditions is difficult to measure (Haverkort and Mac Kerron, 2006), and studies on soil denitrification are scarce, especially in Mediterranean countries. Moreover, the changes in N balance factors and environmental conditions with time have to be taken into account.

6.3.2 LINKING FLOW REGIME AND N EXPORT

In the Mediterranean basins, the hydrological regime has a great influence on sediment and nutrient dynamics in streams (Bisantino et al., 2010; De Girolamo et al., 2015c; Gómez et al., 2009; Welter and Fisher 2016), microbial activities in streambed sediments (Amalfitano et al., 2008), and overall river ecology (Buffagni et al., 2010; Gallart et al., 2012; Larned et al., 2010; Prat et al., 2014).

In the Celone catchment, two aspects of the hydrological regime that may exert a great influence on nutrient dynamics were identified: intermittency and flashiness (how quickly streamflow changes from one magnitude to another after storms) (paragraphs 5.1 and 6.1). From June to December (dry season), it can be observed as a continuum where perennial reaches with low flow (a few liters per second), pools sustained by sub-surface flow, and completely dry reaches longitudinally coexist (De Girolamo et al., 2017a). In this season, rainfall events of moderate or low intensity (<5 mm hr^{-1}) produce isolated pools along the stream channel that remain a few days, after that a high level of N concentrations in water is recorded (i.e. October 2010).

These results are consistent with previous study in Mediterranean rivers (Arce et al., 2013; Von Schiller et al., 2008). Arce et al. (2013) pointed out that during the dry season microbial N activity and the reduced denitrification may lead to nitrate accumulation in streambed sediments, and the rewetting of dry streambed sediments induces an increase of nitrate concentration in water. On the other hand, also the WWTPs effluents discharged into the river have a great influence on nutrient dynamics in this period. Amalfitano et al. (2008) observed that microbial communities are significantly affected by water stress conditions, and there are changes in microbial community structure with a drastic reduction of metabolic activity. Hence, pollutants coming from waste water treatment plants, accumulated on the river bed, could have a low probability to be metabolized. As a result, aquatic sediments can act as a sink and source of nutrients (Aristi et al., 2015).

Flash floods are frequent events in the study area in summer. These events are characterized by high nutrient concentrations, although the contemporaneous streamflow value are modest, and consequently N load is moderate in absolute terms. For instance, on 21st July 2010, when a particularly heavy rainfall was recorded (73.6 mm in an hour), in 15 min the streamflow passed from 0.1 m^3s^{-1} to 4.35 m^3s^{-1} and in the same time interval the TN increased from 3.069 mg $l^{-1}$to 18.6 mg l^{-1}, with TON as predominant form (15.2 mg l^{-1}). This is due to the fact that in summer, when a large part of the basin is constituted by bare soil after the harvesting of durum and winter wheat cultivations, rainfall events are localized in small areas and show a high intensity; runoff generation is mainly due to “infiltration excess” (Kirkby et al., 2011). When overland flow is generated by infiltration excess, flow energy can increase rapidly causing flash flood events with a few hours duration, during which streamflow increase and decrease rapidly and a huge amount of suspended material is transported to the river, flushing the sediments and particulate matter previously accumulated on the river bed (De Girolamo et al., 2015b). In wet season, when most of the basin is covered by vegetation, soils are generally wet, and runoff generation is mainly due to “saturation excess”, a considerable amount of organic and inorganic matter in surface water was found. Few flood events are responsible for nearly 60% of the total annual N load.

In conclusion, after analysing streamflow and concentrations, it can be say that both extreme high and low flow are “critical” time periods for water quality. In the extreme low flow conditions, flow intermittency and the WWTP effluents are responsible for a high level of nitrate concentrations in waters that frequently surpass quality standards (D.M. 260/2010, 2010); floods cause considerable concentrations of organic and inorganic matter eroded from hill slopes and river banks. Hence, our results confirm that riverine export is the result of N input and output in the catchment in addition to the interaction of several factors, among them hydrological processes and flow intermittency (wet-rewetting).

6.4 WATER FOOTPRINT AND WATER FOOTPRINT SUSTAINABILITY ASSESSMENTS

6.4.1 COMPARISON WITH PREVIOUS STUDIES

The current study performs a complete WF assessment of crop production in the Celone watershed (D'Ambrosio et al., 2017b). The results of the WF accounting can be compared to results from earlier studies on the WF, related to the production of similar crop types to those cultivated in the study area (Table 21). We selected those previous studies, which estimated the WF following the calculation methodology proposed by Hoekstra et al. (2011), regardless of the fact that they were conducted on global, national, river basin and field scales.

The comparison of our estimates with those from previous studies shows that the order of magnitude is similar, but the variation range is wide. The differences in the outcomes of the various studies showed in Table 21 can be due to a variety of factors, taken into consideration in the WF calculations, such as type of study area, climate, period of study, model, spatial resolution, data quality, soil, crop yield, planting and harvesting dates, agricultural practices (de Miguel et al., 2015; Lovarelli et al., 2016).

In particular, the climate plays a great influence on WF_{green} and WF_{blue}. Instead, nutrient dynamics and, thus, leaching-runoff fractions (α) mainly depend on the hydrological regime, which for a temporary river system is characterised by a seasonal pattern of drought and flash floods. Hence, differences in the WF_{grey} outcomes (Table 21) primarily are due to different hydrological regimes, as well as to different C_{max} and C_{nat} values (Gil et al., 2017; Liu et al., 2017; Zhuo et al., 2016). The WF_{grey} is, on average, about 10 times higher than the $WF_{grey}{}^{C}$.

Table 21: Comparison of the current study results with those of previous studies. Minimum and maximum values of LUS WFs are reported for the current study. WF_{grey} reports minimum and maximum values obtained considering: i) $N_{RE,mean}$ - $N_{RE,min}$ - $N_{RE,max}$ in equations (27) and (28) for α estimation; ii) C_{max} equal to 3 mg l-1; and iii) C_{nat} equal to 0.4 mg l-1. The WF_{grey}^{C} reports the values obtained considering: i) α equal to 10%; ii) C_{max} equal to 10 mg $^{l-1}$; and iii) C_{nat} equal to 0 mg l^{-1}. Columns for previous studies show results from earlier studies (D'Ambrosio et al., 2017b)

Crop	Current study (m^3 t^{-1})				Previous studies (m^3 t^{-1})			Authors
	WF_{green}	WF_{blue}	WF_{grey}	WF_{grey}^{C}	WF_{green}	WF_{blue}	WF_{grey}	
Crucifers (rapeseed)	889.5	0	2033.9 - 3702.7	320.0	1062 - 2832	0 - 2150	181 - 6617	(Mekonnen and Hoekstra, 2011; Zhuo et al., 2016)
Durum wheat	658.4 - 680.3	0	2332.4 - 3971.3	368.6	216 - 3604	0 - 1478	0 -518	(Chouchane et al., 2015; de Miguel et al., 2015; Mekonnen and Hoekstra, 2011, 2010; Zhuo et al., 2016)
Field bean (broad beans)	64.3 - 96.9	0	146.6 - 261	20.0	1317	205	496	(Mekonnen and Hoekstra, 2011)
Herbage (corn)	57.8 - 65.1	0 - 32.4	201.4 - 361.7	32.0	276 - 1082	0 - 249	187 - 7682	(Bocchiola et al., 2013; Mekonnen and Hoekstra, 2011; Nana et al., 2014; Zhuo et al., 2016)
Legumes	706.9 - 978.6	0	0	0.0	665 - 3180	0 - 395	20 - 734	(de Miguel et al., 2015; Mekonnen and Hoekstra, 2011)
Olive grove	1603.1 - 1972.1	0 - 496.8	3014 - 5328.1	414.3	687 - 8790	330 - 2000	40 -411	(Chouchane et al., 2015; Mekonnen and Hoekstra, 2011; Pellegrini et al., 2016)
Orchard	258.7 - 328.6	0	126.6 - 229.7	21.9	727	147	93	(Mekonnen and Hoekstra, 2011)
Potato	107 - 135.7	0	335.2 - 600.5	53.3	34 - 327	0 - 121	20 - 1002	(Chouchane et al., 2015; de Miguel et al., 2015; Mekonnen and Hoekstra, 2011; Zhuo et al., 2016)
Sugar beet	40.9 - 41.9	13 - 13.1	126.7 - 218	21.6	82 - 306	0 - 52	15 - 1578	(Mekonnen and Hoekstra, 2011; Zhuo et al., 2016)
Sunflower	765.3 - 939.4	0 – 0	2016.5 - 3638.8	333.3	1096 – 3017	145 - 220	121 - 6106	(Mekonnen and Hoekstra, 2011; Zhuo et al., 2016)
Tomato	36.4	52.3	149.1 - 274.3	26.7	2 – 198	19 – 68	10 - 1631	(Chouchane et al., 2015; Evangelou et al., 2016; Mekonnen and Hoekstra, 2011; Zhuo et al., 2016)
Vegetable crop	70.3 - 73.6	46.4 - 57.4	249.1 - 446.8	43.3	0 – 194	0 - 122	0 - 201	(de Miguel et al., 2015; Mekonnen and Hoekstra, 2011)
Vetch (broad beans)	71.9 - 78.5	0	197 - 354.7	26.7	1317	205	496	(Mekonnen and Hoekstra, 2011)
Vineyard	346 - 401.1	0 - 122.2	534.5 - 946.9	85.7	76 - 550	0 - 1080	33 - 87	(Chouchane et al., 2015; de Miguel et al., 2015; Mekonnen and Hoekstra, 2011)
Winter wheat (wheat)	1366.8 - 1439.5	0	2750.4 - 4992.4	416.1	216 - 3604	0 - 1478	0 -518	(Chouchane et al., 2015; de Miguel et al., 2015; Mekonnen and Hoekstra, 2011, 2010; Zhuo et al., 2016)

6.4.2 SUSTAINABILITY ANALYSIS AND RESPONSE FORMULATION, IN ORDER TO ACHIEVE SUSTAINABILITY

With respect to the sustainability analysis, the green water management is sustainable (D'Ambrosio et al., 2017b). Conversely, analysis of the WPL values reveals that surface-water pollution in the Celone river is unsustainable, if WF_{grey} is considered. Also, the watershed results in a low blue water scarcity condition, if the EFR threshold of 0.05 m^3 s^{-1} is used, as established by the river basin authority; however, this result is affected by the EFR considered. Indeed, if it is assumed that EFR accounts for an 80% share of the R_{nat}, significant water scarcity is registered (July 2010 to September 2010).

Therefore, the current study shows how the WF_{grey} and WPL, as well as WS_{blue}, are highly sensitive to the water standards applied. As already mentioned by Liu et al. (2017) and Veettil and Mishra (2016), C_{max}, C_{nat} and EFR values should be standardised for a consistent sustainability assessment. Further research on these issues is needed, therefore.

Since the WF_{grey} and WF_{blue} are not sustainable, as deduced by precautionary WPL and WS_{blue} indices, a response formulation, in order to achieve sustainability, must be defined (D'Ambrosio et al., 2017b). Site-specific fertiliser strategies, which consider soil type, crop development, nutrient dynamics and crop rotational effects, are key to minimising TN leaching and runoff, and thus the WF_{grey} and WPL estimate (Brueck and Lammel, 2016). Since a significant WS_{blue} was registered during the summer months, water withdrawal should generally be avoided. Therefore, irrigation should be averted, and rain-fed crops with high K_S values, such as durum wheat, should be preferred. Alternatively, water productivity could be maximised by applying less irrigation water in a smarter way (Hoekstra et al., 2011).

In achieving the sustainability process, the involvement of local farmers and dealers is essential. Indeed, Mekonnen and Hoekstra (2011) observed that the crop yield is influenced by agricultural management, rather than by the agro-climate under which the crop is grown. This provides an opportunity to decrease the WF, producing larger crop yields using green water. Optimising the crop planting pattern often allows a more sustainable water use to be achieved in arid and semi-arid regions (Davis et al., 2017; Zeng et al., 2012); however, any decision about the crop type, or system to be promoted, should be supported by detailed economic analyses (Lovarelli et al., 2016; Zeng et al., 2012; Zoumides et al., 2014).

6.4.3 REFINEMENTS IN GREY WATER FOOTPRINT ASSESSMENT

The current study points out that WF_{grey} assessments that distinguish between surface water and groundwater are crucial (D'Ambrosio et al., 2017b). Indeed, TN transport into freshwater occurs via surface runoff and leaching, and the use of a single leaching-runoff fraction (α, 10%) does not allow one to differentiate which part refers to the runoff to surface water, and which to the leaching to groundwater (Brueck and Lammel, 2016; Franke et al., 2013). Moreover, the use of the static 10% approach does not take into account site-specific factors, such as the climatic conditions, soil properties and crop management practices that exert a great influence on freshwater pollution.

Therefore, evaluating α values by means of the procedure suggested by Franke et al. (2013), distinguishing between leaching and runoff fractions, and matching these with the results of in-stream monitoring activities with a nitrogen balance quantification, it is possible to estimate two different

fractions (α_L, α_R), as done in this study. Furthermore, the fact that the procedure relies on real on-site measurements that accurately analyse the peak discharges, in addition to the normal and low flow conditions, is an added value. Indeed, according to Liu et al. (2012), indicators such as WF_{grey} and water pollution level (WPL) should be derived from validated model results. This is crucial, especially for Mediterranean basins with temporary river systems, since flood loads constitute the majority of the total annual pollutant loads (De Girolamo et al., 2012a).
Another innovative aspect introduced is the uncertainty related to the load estimation method used for (α_L, α_R) estimation, when flow and concentration measurements are not continuous and simultaneous (D'Ambrosio et al., 2017b). Thus, taking into account the significant discrepancies in the results between four different load estimation methods, three plausible TN riverine export values ($N_{RE,mean}$, $N_{RE,max}$, $N_{RE,min}$) were calculated, and three pairs of (α_L, α_R) for each crop were then identified. In particular, the calibrated runoff fraction (α_R) values (Table 20) are estimated in the range of 0-0.50 for the Candelaro watershed, of which the study area is a sub-basin (Bouraoui et al., 2009).
When $N_{RE,mean}$ and $N_{RE,max}$ are considered, α_L values are equal to zero, since the TN in soil and leaching (L) used for calibration was equal to zero. This surely indicates that runoff is the main component of TN transport into freshwater in the Celone catchment.
Concerning C_{max} values, different values for surface and groundwater were considered, unlike previous WF_{grey} assessments. Moreover, TN good ambient water-quality standards were used, rather than drinking-water standards that correspond to the quality of water at the tap, and not to quality criteria corresponding to good raw water (Hinsby et al., 2008). Instead, the natural background concentrations (C_{nat}) were assumed to be higher than zero, and such an assumption is more realistic than to neglect it (Franke et al., 2013; Hinsby et al., 2008; Liu et al., 2017). The C_{nat} of TN was set to be the same for river and groundwater both, however, since local data were not available (D'Ambrosio et al., 2017b).
Finally, the uncertainty analysis carried out in the current study, and related to α-C_{max}-C_{nat}, highlights the huge variability of WF_{grey} assessment outcomes, depending on the values assigned to the three aforementioned parameters. Therefore, the standardisation of water-quality standards (C_{max}), as well as a harmonisation of α and C_{nat} estimation methods, are indispensable for a consistent and comparable WF_{grey} assessment.

6.4.4 LIMITATIONS OF THE STUDY

The study is affected by some limitations related to the runoff calibration procedure, as well as to the WF assessment methodology (D'Ambrosio et al., 2017b).
With respect to the runoff calibration procedure, CN II values were found to be affected by a high variability for the same LUSs during the study period, as mentioned above. This is in agreement with the results of other studies, which underline the importance of having more than one CN for a watershed (Hjelmfelt, 1991; McCuen, 2002; Soulis and Valiantzas, 2012). Ponce and Hawkins (1996) found possible sources of this high variability to be the effects of the temporal (rainfall intensity) and spatial variability of storm and watershed properties (plant growth), the quality of measured data (flow and precipitation measurements), and the effects of antecedent rainfall and associated soil moisture (AMC), that are assumed to be the primary causes of storm to storm variation (Mishra et al., 2008).

Moreover, the procedure adopted in this study suffers from three limitations:

- 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-day period;
- CN values were determined using only one-year datasets; and
- small events that produce no runoff were not excluded. These limitations could have led to an overestimation of CNII values, higher than those given in the tables of the USDA (1986), as reported by Hjelmfelt (1991) for semiarid watersheds.

The calibration procedure, and CN variability from storm to storm, will be addressed in a further study because it falls outside the scope of the present study, which primarily focuses on the WF assessment.
Limitations of the runoff estimation affect WF_{green} and WF_{blue} assessments, however, since it is a component of the water balance for the root zone.
Other limitations of the overall study relate to the limited time-period analysed, as well as to the discretisation of the watershed into LUSs. Indeed, in the current research, the results for only one specific year (July 2010 – June 2011) were presented because water-quality data were only available for this period. Since the outcomes are affected by the period of data used (Hoekstra et al., 2011), and the study period was wetter than average conditions, water scarcity is estimated according to an optimistic point of view. Hence, an average over multiple years would be more appropriate to represent the general status of water scarcity (Liu et al., 2016; Zhuo et al., 2016). As well, the discretisation of the watershed into LUSs leaves out local factors, such as slope, rainfall intensity and river distance, that influence hydrological processes, besides leaching and runoff fraction (Mekonnen and Hoekstra, 2011; Savvidou et al., 2016). Furthermore, despite the fact that the current study gathered high-quality data, due to the collaboration of local dealers and farmers in providing the necessary agronomic data, it was not possible to assign the actual agricultural practices to each field because of the high fragmentation of land use and adopted management practices within the catchment (D’Ambrosio et al., 2017b). Therefore, the same averaged values were assigned to specific crops throughout the study area, neglecting site-specific information. For all these reasons, the simplified approach adopted in this research provides only a rough estimate.
Other limitations affect specifically WF_{grey} assessment and the WF sustainability assessment. Regarding the WF_{grey}, a conservative estimate was performed, since only TN was considered as a pollutant. Moreover, TN accumulation and degradation processes in the receiving water-bodies were neglected. Therefore, further study should analyse other coexistent pollutants, such as phosphorus and pesticides, in addition to TN, in order to better estimate the actual water dilution requirement (Liu et al., 2017; Mekonnen and Hoekstra, 2011).
Similarly, the sustainability assessment undertaken in this study is limited to assessing the water scarcity and WPL of crop production. A comprehensive assessment should include all the activities carried out in the river basin, such as livestock, domestic and industrial sectors, in order to evaluate the actual environmental sustainability level (de Miguel et al., 2015; Liu et al., 2016; Zeng et al., 2012). Lastly, the WS_{green}, WS_{blue} and WPL were assessed at river-basin level. Consequently, the outcomes do not show differences within the catchment, since all the evaluations are smoothed out, and potential negative impacts could be hidden (Hoekstra et al., 2011). Therefore, the WF sustainability assessment should be performed at the highest level of spatial accuracy as possible, such as grid or sub-basin level (Liu et al., 2012, 2017; Pellicer-Martínez and Martínez-Paz, 2016b).

6.4.5 STRENGTHS AND OPPORTUNITIES OF A COMPLETE WF ASSESSMENT IN SCARCE-WATER COUNTRIES

Despite the limitations of the methodology, a complete WF assessment can be used to track current resource use, highlight the main threats and weakness of resource use, compare different cropping systems, quantify the outcomes of proposed response formulation, and of specific policies undertaken to achieve sustainability (Galli et al., 2012; Pellegrini et al., 2016; Stathatou et al., 2012).

Particularly in Mediterranean basins, characterised by irregular and harsh streamflow fluctuations that exert a great influence on nutrient dynamics (D'Ambrosio et al., 2017; De Girolamo et al., 2012b), the sustainability assessment of blue and grey WFs could be strategic in enhancing water resource allocation and management, and reducing environmental impacts related to fertilisation practices (D'Ambrosio et al., 2017b). Moreover, WF estimates could be used for the development of climate change adaptation policies, as well as for the implementation of the River Basin Management Plans prescribed by the EU Water Framework Directive, as already done in EU countries like Spain and Germany (Aldaya et al., 2010; Zoumides et al., 2014). Indeed, climate change studies underline that Mediterranean regions will experience an increase in temperature and a decrease in precipitation (Abouabdillah et al., 2010). Therefore, the already limited water resources will be compromised, and maintenance strategies should already be in the process of being adopted.

In such a context, the WF is a powerful tool to support the decision-making process, and can be used as a basis for effective policy-setting.

7 CONCLUSIONS

In recent decades, interest in the science and management of Mediterranean temporary streams has increased (D'Ambrosio et al., 2017a). However, only few data on water quantity and quality parameters are generally available. Indeed, the limited financial budget, the not stable river banks and vandalism acts, which are quite common in several countries, make more difficult the monitoring activities in temporary streams than in perennial rivers. Moreover, a detailed and expensive program of water monitoring should be conducted for the long term including flood events in order to best understand all the processes acting in the temporary river basin, since hydrological processes and physical aspects (slope, soil properties, climate, etc.) are generally highly variable in space and time. Due to the paucity of data in most watersheds of the Mediterranean region is difficult to characterise and classify the hydrological regime, to evaluate pollutant loads delivered to the river, to allocate loads between different sources (point and non-point) and to define the current status and use of surface waters. However, these tasks are fundamental to identify a programme of measures at basin level for achieving the environmental objectives of the Water Framework Directive (De Girolamo et al., 2017b).

In this work, the practicality of methodologies based on established techniques and data which is easy to use by technicians and water resources managers, were assessed using a case study. In particular, four little addressed topics for Mediterranean watersheds were analyzed.

1) New approaches to characterise and classify the hydrological regime of temporary streams, different from that applied to perennial streams, were defined (D'Ambrosio et al., 2017a). The hydrological regime of a temporary river system was analysed through a number of HIs. A selection of essential and easy-to-measure catchment characteristics (gauging station elevation, land use, catchment area, mean annual precipitation, hydraulic conductivity and available water content) were used to determine the HIs of ungauged streams in the study area fitting statistically significant relationships.
2) The temporal variability of N loads at the basin outlet was studied from 2010 to 2011, considering the contribution of flood events, the normal and low flow to the total annual load (De Girolamo et al., 2017b).
3) A first attempt to evaluate the N balance in a basin with a limited data availability was made and anthropogenic and natural input and output of N were assessed (De Girolamo et al., 2017a).
4) A complete WF assessment of crop production at a river-basin scale. The methodological approach proposed by the Water Footprint Network was applied to the Celone watershed, characterised by a temporary river system (D'Ambrosio et al., 2017b; D'Ambrosio et al., 2017c). The WF_{green} and WF_{blue} were evaluated, performing a soil-water balance on a 10-day time-interval. The grey component of the WF was quantified by means of the results from in-stream monitoring activities, and considering two different combinations of α, C_{max} and C_{nat} values for surface water (i.e., calibrated value - 3 mg l^{-1} to 0.4 mg l^{-1} and 10% – 10 mg l^{-1} to 0 mg l^{-1}). Moreover, analysis of environmental sustainability of green, blue and grey water resource management was performed at the basin level. Since WF_{grey} and WF_{blue} were found not to be sustainable, response formulations to achieve sustainability of water and land use in water-scarce countries were finally defined.

The main conclusions drawn from this study are as follows:

1a. The metrics commonly used in eco-hydrological studies are redundant. Thus, a PCA-based methodology can be used to identify a small subset of metrics that properly represent the flow regime of a particular river basin.

1b. The MAJ, MAMar, DH4, DH5, FL1, RA2, SD6 and the MF accounted for most of the variance found in the 37 indicators analysed. This small subset of HIs covers the main regime characteristics such as magnitude, duration, frequency and timing.

1c. Linear models using selected catchment characteristics for estimate HIs of ungauged streams fail to properly describe some indicators. However, when using a different kind of model such as second-order polynomials, all the HIs results were highly significant. Hence, second-order regression models permit the estimation of some relevant aspects of a hydrological regime in the absence of measured data.

1d. Knowledge of the hydrological processes acting in the study area as well as the anthropogenic pressures are necessary before applying a regression model.

1e. MF and SD6 indicators can be broadly used to differentiate streams within the study area by their degree of temporariness because the latter has great influence on biota.

1f. Using a regression model to calculate the metrics (MF and SD6), it is possible to classify ungauged river reaches with moderate or low impacts in the study area.

2a. N loss from surface runoff is essentially a winter process, which shows a marked seasonality related to rain patterns and agricultural practices (fertilizers application).

2b. Point sources have a great impact in terms of nutrient concentrations for the duration of low flow, while loading are negligible.

2c. The importance of flood event contributions to the annual N loadings is clearly demonstrates. Indeed, few flood events were responsible for nearly 60% of the total annual loads.

2d. Since in temporary rivers magnitude and timing of floods can vary largely, further research is needed to better characterize nutrients transport during these events and to analyse the relationships among different forms of N to identify mitigation management actions.

2e. The presence of high level of N in surface water forewarns a potential N surplus in the watershed.

3a. N balance quantification is not an easy task. Data acquisition and handling are the first challenge to overcome in such studies in the Mediterranean Region.

3b. Based on one-year of observations an N surplus was found, which is mainly due to fertilizers and manure spreading. The difference between input (fertilizers, animal farming, atmospheric deposition, biological fixation) and output (crop uptake, volatilization and denitrification) is quite high if compared to other watersheds in Southern Italy, and unexpected for the study area that is in part a rural area with conventional agriculture. This demonstrates the importance of such detailed studies also in areas apparently not heavily impacted.

3c. The hydrological regime has a relevant role in N transport and dynamics. In the study area, N losses are essentially a winter process; major floods cause considerable addiction of organic and inorganic matter to the surface waters. Hence, in order to quantify N loads, monitoring activities have to include floods. On the other hand, dry periods can be critical in term of N concentrations. In fact, the flash flood events occurring after a dry period remobilize a large amount of nutrients deposited on the river bed during the extreme low flow and are characterized by high concentrations of particulate matter. The intermittency of flow in channel network has important implications for N dynamics and it is responsible for high concentrations in the rewetting phase.

3d. Further analysis are required to reduce uncertainty in nutrient balance calculations. In particular, denitrification processes in soils and river network should be deeply investigated, as well as the influence of hydrological regime of intermittent stream on N transport and metabolism.

4a. Green water represents a substantial part of the total WF and is fundamental for crop production in semi-arid regions.

4b. WF_{grey} and WPL, as well as WS_{blue}, are highly sensitive to the water standards applied. Hence, further research on these issues is needed, in order to standardise C_{max}, C_{nat} and EFR definition for a consistent sustainability assessment.

4c. Local data and measurements are fundamental, and caution should be used when, in the absence of actual measurements, literature data are selected for estimating grey water, especially in Mediterranean watersheds.

4d. Being WF_{grey} and WF_{blue} not sustainable, as deduced by precautionary WPL and WS_{blue} indices, response formulation in order to achieve sustainability must be defined. Thus, site-specific fertilizer strategies are key to minimize TN leaching and runoff. Since a significant WS_{blue} is registered during summer months, water withdrawal should generally be avoided. Therefore the irrigation should be avert and rain fed crops with high K_S value, as durum wheat, should be preferred.

4e. The sustainability assessment of blue and grey WF could be strategic for enhance water resource allocation and management and reduce environmental impacts related to fertilization practices especially in the Mediterranean basins, characterised by an irregular and harsh streamflow fluctuations that exerts a great influence on nutrient dynamics.

The current study focused on specific temporary watersheds (i.e. Candelaro – Carapelle - Cervaro for the first topic and Celone for the rest three) but the method used can be applied to other catchment as well if water quality and quantity measurement are available. Moreover, these catchments can be considered representative of most rural basins in the Mediterranean Region, in term of climate, land use and data availability. Hence, the methodologies, the insights gained from this research and the analysed shortcomings could support local authorities in the decision making process for effective agricultural policy setting and water planning, fostering the implementation of the Water Framework Directive.

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WET CONDITION


DRY CONDITION