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Progressive development of a hydrologic and inorganic nitrogen conceptual model to improve the understanding of small Mediterranean catchments behaviour

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Al nonno Uber,
e tutta la famiglia

“*Scientific understanding proceeds by way of constructing and analysing models of the segments or aspects of reality under study. The purpose of these models is not to give a mirror image of reality, not to include all its elements in their exact sizes and proportions, but rather to single out and make available for intensive investigation those elements which are decisive. We abstract from non-essentials, we blot out the unimportant to get an unobstructed view of the important, we magnify in order to improve the range and accuracy of our observation. A model is, and must be, unrealistic in the sense in which the word is most commonly used. Nevertheless, and in a sense, paradoxically, if it is a good model it provides the key to understanding reality*”

(Baran and Sweezy, 1968)

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Resumen

El conocimiento de los procesos hidrológicos es esencial para la gestión de los recursos hídricos tanto desde el punto de vista cuantitativo (crecidas o sequías) como desde el punto de vista cualitativo (contaminación).
El funcionamiento hidrológico de las cuencas mediterráneas es aún bastante desconocido a pesar de los diferentes estudios realizados desde hace una veintena de años. Los progresos realizados en la identificación y modelización de los procesos hidrológicos corresponden casi en la totalidad a investigaciones realizadas en clima templado-húmedo (Bonell y Balek, 1993; Buttle, 1994). Según Bonell (1993), esta falta de información fuerza a la “transferencia de resultados”, a pesar de la necesidad evidente de desarrollar aproximaciones diferentes, principalmente en el ámbito de la modelización (Pilgrim et al. 1988).
En relación a la modelación hidrológica, los estudios disponibles (Durand et al., 1992; Parkin et al., 1996; Piñol et al., 1997 entre otros) muestran serias dificultades para reproducir las primeras crecidas de otoño, después del periodo estival seco. En este tipo de cuencas parece difícil modelizar correctamente uno o más años hidrológicos completos con un solo juego de parámetros (Piñol et al., 1997, Bernal et al., 2004).
El clima mediterráneo está caracterizado por una dinámica estacional muy marcada del régimen de precipitaciones y de la evapotranspiración, que favorece la alternancia durante el año de periodos secos y húmedos. Esto modifica fuertemente el estado hidrológico de la cuenca, que deriva un comportamiento hidrológico complejo y no-lineal (Piñol et al. 1999).
La necesidad de comprender el funcionamiento hidrológico de un sistema responde a dos cuestiones importantes: por un lado es el procedimiento más indicado para proporcionar elementos útiles a la gestión integrada de los recursos hídricos y por otro lado es fundamental para la modelación del comportamiento de nutrientes, por ejemplo el nitrato, dada su alta solubilidad.
En las últimas décadas, la lixiviación de nitrato ha recibido una gran atención debido al incremento tanto de la tasa de deposición atmosférica

como del aporte difuso procedente de las zonas agrícolas (Vitousek et al., 1979). Cuantificar el flujo de nitrógeno y los mecanismos que lo gobiernan a escala de cuenca resulta esencial para poder predecir los efectos que se producirían en la calidad de las aguas debido a cambios de uso del suelo o al cambio climático (Payraudeau et al., 2001).

Esta problemática, de por si compleja, resulta aún más difícil cuando se trata de cuencas de clima Mediterráneo caracterizadas por un alternancia de periodos secos y húmedos que se traduce en un comportamiento hidrológico y biológico altamente no lineal (Bernal et al., 2004; Medici et al., 2008).

Variaciones en la disponibilidad de algún recurso pueden alterar significativamente el funcionamiento de un ecosistema, especialmente con respecto a la dinámica de la población bacteriana y de los ciclos de materia orgánica y de nutrientes. En este sentido, los sistemas áridos y semiáridos representan medios en los que la disponibilidad de los recursos, como por ejemplo el agua, es intermitente y donde tal disponibilidad se manifiesta como "pulsos" en medio de largos periodos de escasez de recursos (Schwinning et al., 2004a).

La tarea de desarrollar modelos, parsimoniosos y robustos, con los que interpretar y predecir el movimiento del nitrógeno inorgánico en una cuenca de tipo Mediterráneo resulta complicada pero extremadamente necesaria (Neal et al., 2002, Liu et al., 2005).

Los modelos que tratan de describir el comportamiento y destino de los nutrientes en el suelo suelen ser necesariamente complejos dado que intentan reproducir todos los principales factores y procesos involucrados para entender su importancia relativa y evaluar su influencia en la respuesta de la cuenca en caso de cambios ambientales (Dean et al., 2009). Sin embargo, hay que tener en cuenta que tales modelos siempre representarán una simplificación de la realidad. Tales simplificaciones son fuentes de incertidumbre y la confiabilidad de un modelo y su robustez obviamente dependerán de la bondad de las hipótesis asumidas. A este propósito, el análisis de sensibilidad general es una metodología que permite explorar las respuestas de un modelo sobre toda una región significativa del espacio de los parámetros.

El caso de estudio de esta tesis doctoral es la cuenca de Fuirosos, situada en la vertiente norte de la Sierra Litoral Catalana, cerca de Barcelona (España). Fuirosos es una cuenca de aproximadamente 13 km^2, que drena un río intermitente.

La primera parte de la investigación se ha centrado en la modelación hidrológica. El enfoque adoptado consiste en una evolución progresiva de la percepción del funcionamiento hidrológico de la cuenca, que se traduce en un perfeccionamiento sucesivo del modelo conceptual adoptado para simular el caudal observado.

El primer modelo adoptado para describir el comportamiento hidrológico de la cuenca de Fuirosos es un modelo agregado que incluye tres distintas respuestas hidrológicas (LU3). El análisis de los resultados obtenidos con el modelo LU3 llevó a introducir un tanque más en el esquema conceptual adoptado para distinguir entre dos tipos de respuestas lentas (o flujos base) de la cuenca, obteniendo así el modelo (LU4). El siguiente paso fue aplicar esta versión agregada, a cuatro respuestas, de manera semidistribuida. El nuevo esquema conceptual (SD4) incluye la variabilidad espacial de la evapotranspiración potencial, introduciendo en su cómputo la orientación característica de cada unidad hidrológica representativa (HRU) y su cubierta vegetal. El modelo SD4 también incluye en su esquema conceptual las cuatro pequeñas balsas presentes en la cuenca. Finalmente, el modelo conceptual semidistribuido SD4 se ha ampliado incluyendo un tanque que representa la zona de ribera, obteniendo así el modelo SD4-R, con el cual se obtuvo el mejor ajuste a los tres años de caudales observados (Nash & Sutcliffe efficiency index =0.78).

Los resultados evidenciaron la importancia de los cambios rápidos del nivel freático en la zona de ribera y de la formación de un acuífero colgado somero en el interfaz entre el suelo y la roca madre granítica meteorizada. Por otro lado, el proceso de transpiración desde los dos acuíferos (el colgado y la zona permanentemente saturada) y la variabilidad espacial de la evapotranspiración también resultaron fundamentales para representar correctamente la respuesta de la cuenca.

Los modelos desarrollados han sido testados de acuerdo con un proceso de validación tanto temporal como espacial.

La segunda parte del trabajo describe el acople de un modelo de nitrógeno inorgánico a los modelos de lluvia-escorrentía anteriormente desarrollados. Los modelos así obtenidos se denominan: LU4-N agregado; LU4-R-N semidistribuido (2 HRU); SD4-R-N semidistribuido (4 HRU). El modelo de nitrógeno adoptado proporciona una descripción simplificada del ciclo del nitrógeno en el suelo, incluyendo los procesos de mineralización, nitrificación, inmovilización bacteriana, desnitrificación, absorción por parte de las plantas y finalmente adsorción y desorción del amonio. También se han incluido los procesos de nitrificación y desnitrificación en el acuífero colgado superficial, considerando que tuvieran un rol fundamental para la simulación de las concentraciones de nitrato y amonio durante la curva de recesión del hidrograma. Además, se han incluido umbrales de humedad del suelo que determinan la dinámica de los procesos que componen el ciclo del nitrógeno. Los resultados obtenidos sugieren que los procesos de transformación del nitrógeno están muy influenciados por el régimen de precipitación, lo cual se refleja en un comportamiento a ‘pulsos’. La zona de ribera resultó ser un elemento fundamental para la simulación del nitrato y se ha evidenciado su papel tanto como posible fuente como de sumidero de nitrato, dependiendo de la época del año y de las condiciones de humedad.

En la última fase de este trabajo, los modelos de simulación de nitrógeno inorgánico desarrollados en esta tesis doctoral (LU4-N, LU4-R-N y SD4-R-N) han sido sometidos a un extenso análisis de sensibilidad general de acuerdo a la metodología conocida como ‘*General Sensitivity Analysis*’

(GSA, Hornberger and Spear, 1980) y '*Generalised Likelihood Uncertainty Estimation*' (GLUE, Beven and Binley, 1992), basadas en 100.000 simulaciones de Monte Carlo. El propósito del estudio fue analizar si el aumento progresivo de parámetros, y por lo tanto de la complejidad de los modelos, se traduce en una mayor capacidad efectiva para reproducir el comportamiento hidrológico y del nitrógeno inorgánico observado en la cuenca de Fuirosos. Los resultados de este análisis apuntan a que el modelo más complejo SD4-R-N es el más adecuado para la simulación tanto del caudal como del nitrógeno inorgánico en la cuenca de Fuirosos.

Resum

El coneixement dels processos hidrològics és essencial per a la gestió dels recursos hídrics, tant des del punt de vista quantitatiu (crescudes o sequeres) com des del punt de vista qualitatiu (contaminació).
El funcionament hidrològic de les conques mediterrànies és encara prou desconegut a pesar dels diversos estudis realitzats des de fa una vintena d'anys. Els progressos realitzats en la identificació i la modelització dels processos hidrològics corresponen quasi en la totalitat a investigacions realitzades en clima temperat-humit (Bonell i Balek, 1993; Buttle, 1994). Aquesta falta d'informació, segons Bonell (1993) força a la "transferència de resultats", a pesar de la necessitat evident de desenvolupar aproximacions diferents, principalment en l'àmbit de la modelització (Pilgrim *et al*., 1988).
Pel que fa a la modelització hidrològica, els estudis disponibles (Durand *et al.,* 1992; Parkin *et al*., 1996; Piñol *et al*., 1997, entre d'altres) mostren dificultats serioses per a reproduir les primeres crescudes de la tardor, després del període estival sec. Per a aquestes conques pareix difícil modelitzar correctament un o més anys hidrològics complets amb un sol joc de paràmetres (Piñol *et* al., 1997, Bernal *et al*., 2004).
El clima mediterrani està caracteritzat per una dinàmica estacional molt marcada del règim de precipitacions i de l'evapotranspiració, que afavoreix l'alternança durant l'any de períodes secs i humits. Això modifica fortament l'estat hidrològic de la conca, de la qual cosa deriva un comportament hidrològic complex i no lineal (Piñol *et al.,* 1999).
La necessitat de comprendre el funcionament hidrològic d'un sistema respon a dos qüestions importants: d'una banda, és el procediment més indicat per a proporcionar elements útils a la gestió integrada dels recursos hídrics, i d'una altra banda, és fonamental per a la modelització del comportament de nutrients, per exemple el nitrat, donada la seua alta solubilitat.
En les últimes dècades, la lixiviació de nitrat ha rebut una gran atenció a causa de l'increment tant de la taxa de deposició atmosfèrica com de

l'aportació difusa procedent de les zones agrícoles (Vitousek *et al*., 1979). Quantificar el fluix de nitrogen i els mecanismes que el governen a escala de conca resulta essencial per a poder predir els efectes que es produirien en la qualitat de les aigües a causa de canvis d'ús del sòl o pel canvi climàtic (Payraudeau *et al*., 2001).

Aquesta problemàtica, de per si complexa, resulta encara més difícil quan es tracta de conques de clima mediterrani caracteritzades per un alternança de períodes secs i humits, que es tradueix en un comportament hidrològic i biològic altament no lineal (Bernal *et al*., 2004; Medici *et al.,* 2008).

Variacions en la disponibilitat d'algun recurs poden alterar significativament el funcionament d'un ecosistema, especialment respecte a la dinàmica de la població bacteriana i dels cicles de matèria orgànica i de nutrients. En aquest sentit, els sistemes àrids i semiàrids representen medis en què la disponibilitat dels recursos, com per exemple l'aigua, és intermitent i on aquesta disponibilitat es manifesta com "polsos" al mig de llargs períodes d'escassetat de recursos (Schwinning *et al.,* 2004a).

La tasca de desenvolupar models, parsimoniosos i robustos, amb què interpretar i predir el moviment del nitrogen inorgànic en una conca de tipus mediterrani, resulta complicada però extremadament necessària (Neal *et al*., 2002, Liu *et al*., 2005).

Els models que tracten de descriure el comportament i la destinació dels nutrients en el sòl solen ser necessàriament complexos, atès que intenten reproduir tots els principals factors i processos involucrats per a entendre'n la importància relativa i avaluar-ne la influència en la resposta de la conca en cas de canvis ambientals (Dean *et al.*, 2009). No obstant això, cal tenir en compte que aquests models sempre representaran una simplificació de la realitat. Tals simplificacions són fonts d'incertesa, i la confiabilitat d'un model i la seua robustesa, òbviament, dependran de la bondat de les hipòtesis assumides. En aquest sentit, l'anàlisi de la sensibilitat general és una metodologia que permet explorar les respostes d'un model sobre tota una regió significativa de l'espai dels paràmetres.

El cas d'estudi d'aquesta tesi doctoral és la conca de Fuirosos, que es troba situada a la vessant nord de la Serra Litoral Catalana, prop de Barcelona (Espanya). Fuirosos és una conca aproximadament de 13 km^2, que drena un riu intermitent.

La primera part de la investigació s'ha centrat en la modelització hidrològica. L'enfocament adoptat consisteix en una evolució progressiva de la percepció del funcionament hidrològic de la conca de Fuirosos, que es tradueix en un successiu perfeccionament del model conceptual adoptat per a simular el cabal observat.

El primer model adoptat per a descriure el comportament hidrològic de la conca de Fuirosos és un model agregat que inclou tres distintes respostes hidrològiques (LU3). L'anàlisi dels resultats obtinguts amb el model LU3 va portar a introduir un tanc més en l'esquema conceptual adoptat per a distingir entre dos tipus de respostes lentes (o fluixos base) de la conca, i així s'obtingué el model LU4. El següent pas va ser aplicar aquesta versió agregada a quatre respostes, de manera semidistribuïda. El nou esquema conceptual (denominat SD4) inclou la variabilitat espacial de l'evapotranspiració potencial introduint en el seu còmput l'orientació característica de cada unitat hidrològica representativa (HRU) i la seua coberta vegetal. El model SD4 inclou en l'esquema conceptual també les quatre petites basses presents a la conca. Finalment, el model conceptual semidistribuït SD4 s'ha ampliat incloent-hi un tanc que representa la zona de ribera, i així s'ha obtingut el model SD4-R, amb el qual s'ha aconseguit el millor ajust als tres anys de cabals observats (Nash & Sutcliffe efficiency index = 0,78).

Els resultats han evidenciat la importància dels canvis ràpids del nivell freàtic de la zona de ribera i de la formació d'un aqüífer penjat succint a la interfície entre el sòl i la roca mare granítica meteoritzada. D'altra banda, també el procés de transpiració des dels dos aqüífers (el penjat i la zona permanentment saturada) i la variabilitat espacial de l'evapotranspiració van resultar fonamentals per a representar correctament la resposta de la conca.

Els models desenvolupats han sigut verificats tant d'acord a un procés de validació temporal com espacial.

La segona part del treball descriu l'acoblament d'un model de nitrogen inorgànic als models de pluja-vessament desenvolupats anteriorment. Els models obtinguts així es denominen: LU4-N agregat, LU4-R-N semidistribuït (2 HRU) i SD4-R-N semidistribuït (4 HRU). El model de nitrogen adoptat proporciona una descripció simplificada del cicle del nitrogen al sòl incloent-hi els processos de mineralització, nitrificació, immobilització bacteriana, desnitrificació, absorció per part de les plantes i, finalment, adsorció i desorció de l'amoni. S'hi han inclòs també els processos de nitrificació i desnitrificació a l'aqüífer penjat superficial, considerant que tingueren un rol fonamental per a la simulació de les concentracions de nitrat i amoni durant la corba de recessió de l'hidrograma. A més, s'hi han inclòs llindars d'humitat del sòl que determinen la dinàmica dels processos que componen el cicle del nitrogen.

Els resultats obtinguts suggereixen que els processos de transformació del nitrogen estan molt influenciats pel règim de precipitació, la qual cosa es reflecteix en un comportament a *polsos*. La zona de ribera va resultar un element fonamental per a la simulació del nitrat, i s'ha evidenciat el paper que té tant com a possible font com d'albelló de nitrat d'acord amb l'època de l'any i les condicions d'humitat.

En l'última fase del treball, els models de simulació de nitrogen inorgànic desenvolupats en aquesta tesi doctoral (LU4-N, LU4-R-N i SD4-R-N) s'han sotmès a una extensa anàlisi de sensibilitat general d'acord a la metodologia coneguda com a General Sensitivity Analysis (GSA, Hornberger and Spear, 1980) i Generalised Likelihood Uncertainty Estimation (GLUE, Beven and Binley, 1992), basades en 100.000 simulacions de Muntanya Carlo. El propòsit de l'estudi ha sigut analitzar si l'augment progressiu de paràmetres, i per tant de la complexitat dels models, es tradueix en una major capacitat efectiva per a reproduir el comportament hidrològic i del nitrogen inorgànic observat a la conca de Fuirosos. Els resultats d'aquesta anàlisi apunten que el model més complex SD4-R-N és el més adequat per a la simulació tant del cabal com del nitrogen inorgànic a la conca de Fuirosos.

Summary

A better knowledge of hydrological processes is essentials for water resources management in terms of water quantity (floods and droughts) as well as water quality (pollution).

The hydrological functioning of Mediterranean systems is still largely unknown despite several studies have been carried out during the last twenty years. Progresses in the identification and modelling of hydrological processes are almost entirely due to research in temperate-humid climate (Bonell y Balek, 1993; Buttle, 1994). According to Bonell (1993), the lack of knowledge forces to ‘the transfer of results’ in spite of the clear need to develop different approaches particularly concerning catchment modelling (Pilgrim et al. 1988).

Concerning the hydrological modelling, the available studies (Durand et al., 1992; Parkin et al., 1996; Piñol et al., 1997 among others) show serious models difficulties in reproducing the first autumnal discharge events, just after the dry summer period. Moreover, generally it seems difficult to model the hydrological behaviour of Mediterranean systems with just one set of parameters (Piñol et al., 1997, Bernal et al., 2004).

Mediterranean climate is characterized by a marked seasonality of rainfall and evapotranspiration processes, which produces alternating wet and dry periods throughout the year. This strongly modifies catchment moisture conditions, which leads to a complex and non linear hydrological behaviour (Piñol et al. 1999).

The need to understand the hydrological functioning of a system responds to two important issues: one is the most appropriate procedure to provide useful elements for the integrated management of water resources and at the same time it is essential for modelling the behaviour of nutrients such as nitrate, due to its high solubility.

During the last decades, nitrate export has become a major concern in river systems because of increases in both atmospheric deposition of nitrogen and diffuse transport from agricultural land uses (Vitousek et al., 1979). Quantifying inorganic nitrogen loads and the mechanisms that govern its dynamic at catchment scale is essential to predict the effect that would occur in water quality due to changes in land use or climate (Payraudeau et al., 2001).

Water quality modelling, which is generally a complex issue, is even more difficult when it concerns Mediterranean systems, characterized by alternating wet and dry conditions that lead to highly non-linear hydrological and biological behaviours (Bernal et al., 2004; Medici et al., 2008). In fact, the variation in the availability of some resource can significantly alter the ecosystem functioning, especially with respect to bacterial population dynamics and organic matter and nutrients cycle. To this end, arid and semiarid environments represent systems in which the availability of resources such as water, is intermittent and where such availability is represented by 'pulses' within long dry periods (Schwinning et al., 2004a).

The task of developing parsimonious and robust models with which to understand and predict the movement of inorganic nitrogen in Mediterranean-type catchments is difficult but extremely necessary (Neal et al., 2002, Liu et al., 2005). Dynamic, process-based models of pollutant sources and catchment dynamics are necessarily complex because they attempt to describe all factors and processes so that the relative importance of these may be understood and investigated in response to environmental change (Dean et al., 2009). However, models will always necessarily be simplification of reality. These simplifying assumptions are a source of uncertainty in a model, and the robustness of any model application will be dependent upon the validity of the assumptions made. Sensitivity analysis provides model users with information regarding the effect of model parameters on the resultant model prediction.

The study case of this PhD thesis is the Fuirosos catchment that is located in the northern slopes of Catalan Littoral Range, near Barcelona (Spain). The drainage area at the Fuirosos flowgauge station is approximately 13 km^2 and it drains an intermittent stream.

The first part of this research has been focused on the catchment hydrological modelling. A progressive perceptual understanding approach was used in order to identify a model structure able to represent the non-linear behaviour of the hydrological cycle in a small intermittent Mediterranean stream.
The initial lumped model structure consisting in a series of three connected water tanks (LU3) progressed to a model with four tanks (LU4), and finally to a semidistributed model structure (SD4) in which spatial variability of the evapotranspiration according to the vegetation cover and to the local aspect was considered. In the final model structure, which gave the best fit (Nash-Sutcliffe efficiency index = 0.78), an additional tank representing the riparian zone was included (SD4-R). Results showed that the abrupt changes of the riparian water table during summer and the formation of a perched water table during the transition from dry to wet conditions were the main mechanisms leading to the non-linear hydrological behaviour. The transpiration process from the saturated zone and the spatial variability of evapotranspiration resulted key factors to successfully represent the annual water balance. The spatial and temporal validations carried out for each of the four model structures considered in this study supported the hypothesis adopted during the calibration process.
The aim of the second part of this work was to couple a nitrogen (N) sub-model to already existent hydrological lumped (LU4-N) and semi-distributed (LU4-R-N and SD4-R-N) conceptual models, to improve our understanding of the factors and processes controlling nitrogen cycling and losses in Mediterranean catchments. The N model adopted provides a simplified conceptualization of the soil nitrogen cycle considering mineralization, nitrification, immobilization, denitrification, plant uptake, and ammonium adsorption/desorption. It also includes nitrification and denitrification in the shallow perched aquifer. We included a soil moisture threshold for all the considered soil processes. The results suggested that all the nitrogen processes were highly influenced by the rain episodes and that soil

microbial processes occurred in pulses stimulated by soil moisture increasing after rain. The riparian zone was a key element to simulate the catchment nitrate behaviour and our simulation highlighted it as a possible source or sink of nitrate depending on the period of the year and the soil moisture conditions.

In the last part of the work the developed models (LU4-N, LU4-R-N y SD4-R-N) have been examined according to an extensive general sensitivity analysis based on 100,000 Monte Carlo simulations (GSA, Hornberger and Spear, 1980 and GLUE, Beven and Binley, 1992). The aim of this part of the study was to determine if additional model complexity actually gives a better capability to model the hydrology and nitrogen dynamics of the Fuirosos catchment. The results obtained highlighted the most complex structure (SD4-R-N) as the most appropriate one representing the non-linear behaviour of this small Mediterranean catchment.

2

General Introduction

2.1 Research framework

Numerous mathematical models have been developed to describe discharge and nitrogen dynamics in cool temperate river-systems. It has been shown that concepts and ideas developed by modellers for humid climates usually fail when applied to semi-arid regions (e.g.: Bernal et al., 2004) and lead in many cases to unsatisfactory results (Bonell, 1993). Therefore, further work is needed to understand and model the main processes controlling water and nitrogen cycle in Mediterranean and semi-arid forested ecosystems since these systems are not well understood (Avila et al., 1995; Wade et al., 2004; Bernal et al., 2005; Gelfand et al, 2008;).

The case study presented in this thesis is a small forested catchment named Fuirosos (Catalonia, Spain), which has a Mediterranean climate characterized by a high hydrological intra and inter-annual variability. All the data available for this work were provided by the Universitat de Barcelona, Departament d'Ecologia and part of them has been collected in the framework of a European project, named NICOLAS (Nitrogen Control by Landscapes, ENV4-CT97-0395).

This study has its origins in a previous work that aimed to simulate hydrology, nitrate and ammonium dynamics of the Fuirosos catchment (Bernal et al., 2004) applying the INCA model (Whitehead et al., 1998 and Wade et al., 2002). INCA is a process-based semi-distributed model developed for humid climates and the model has been widely shown to simulate the hydrological and nitrogen dynamics of temperate ecosystems (Wade et al., 2004). In the Fuirosos catchment, however, a single parameter set for three hydrological years fails to capture the intrinsic intra and inter-annual variability observed in the measured flow and streamwater nitrate concentrations. Thus, the main aim of the present work is to develop an improved model of Mediterranean catchment flow and nitrogen dynamics, even if '…defining a better model is, itself, a difficult issue' (Beven et al., 2009, Preface).

The underlying idea of this work is that model applications are part of a learning process, not just about the models themselves, but in particular about the environmental system we want to model. Beven (2001) pointed out that there is much modelling that is carried out mainly for research purposes as a means of formalizing knowledge about environmental systems. In the same way, Blöschl et al. (1995) stated that in general, investigative models are more complex in structure and their predictions may be less robust, but they allow better insight into system behaviour. In fact, learning from model applications to come "closer" to the real factors and processes and how they integrate is an important and recognized way of developing an area of science.

However, there are limitations on how far we can take this process and these limitations have important implications for modelling practice and model predictions reliability. This means that there will be uncertainties in the predictive capabilities of environmental models and therefore a risk of being wrong in making predictions (Beven, 2009). To this end, sensitivity analysis provides an assessment of model robustness, giving information regarding the effect of model parameters and input data on the resultant model output. These types of analyses often lead also to improve the mathematical model, and help learning about the underlying perceptual model, or at least show us where gaps in our knowledge are most severe and are most strongly affecting prediction uncertainty (Wagener et al., 2007).

Hydrological modelling of the Fuirosos catchment was initiated with the aims of gaining an understanding of both hydrological and biogeochemical processes and of the interaction between the water and the nitrogen cycle. Hence, this study was started with a basic model and then progressively modified in a thoughtful way to see if the model could be made more consistent with the perceptions of how the hydrology and inorganic nitrogen dynamic of the catchment in question worked, taking into account fieldworks and literature data about Mediterranean and semi-arid basins. All the models of this thesis have been developed in MS Office Excel 2003 and afterwards 2007.

2.2 Mediterranean climate

The Mediterranean climate is characterised by warm, dry summers and wet winters. The term Mediterranean-climate includes regions that share a similar climate regime all around the world from the Pacific Coast of North America (latitude 31º - 41ºN) to parts of West and of South Australia (latitude 32º - 35º S), the central Chilean coast (latitude 32º - 41º S) or South Africa (latitude 33º - 35º S) (Gasith and Resh 1999). All these regions are characterized by quite different annual precipitation regimes form arid (annual precipitation <250 mm) to humid ones (annual precipitation > 1000 mm). However, the marked seasonality and huge inter and intra-annual precipitation variability is a common feature for all of them.
Mediterranean catchments contrast with temperate-humid catchments in that for the former the annual potential evapotranspiration is generally greater than the mean annual precipitation (250 mm < annual precipitation < 1000 mm, Strahler and Strahler 1989), which typically leads to drought period during summer. The total amount of water that can be evapotranspirated from these catchments can account for the major part of the annual precipitation (up to more than 80%). The accurate characterisations of the temporal and spatial dynamics of evapotranspiration are required to understand the water balance of Mediterranean catchments (e.g., Ceballos and Schnabel 1998). On the contrary, in temperate regions, the evapotranspiration generally accounts for 30 to 60% of annual precipitation (e.g. Neal and Kirchner 2000, Wade et al. 2002). Furthermore, for Mediterranean regions, the variability in the amount and distribution of precipitation is much higher than in temperate

regions, which is reflected by large variability in the annual water balance (Piñol et al 1991; Ceballos and Schnabel 1998, Latron, 2003, Bernal, 2006). The extremely variable precipitation regime in Mediterranean climates results in a complex stream hydrology reflected in a characteristic seasonal pattern. Namely, three recognizable periods during the same hydrological year can be defined: a long dry season; a wetting-up period (during which large rainfall events may produce little or no response at the flow gauge station); and finally a wet season (Piñol et al., 1997; Gallart et al., 2002; Latron 2003). In particular, the wetting-up period is a critical point for the hydrological and hydrochemical functioning of Mediterranean catchments (Durand et al., 1993).

The Mediterranean climate imposes an environmental template to ecosystems where the key factor is water availability. In this sense, soil processes in Mediterranean regions are limited by soil moisture and not by low temperature, as in humid catchment. In fact, several authors have stated that alternate dry and humid conditions influence the soil microbial activity. In particular, Schwinning et al. (2004a, 2004b) described a "pulse dynamic" in arid and semi-arid ecosystems and Rey et al. (2002) reported that whenever soil moisture had a limiting effect on soil respiration, soil respiration responded quickly and sharply to each rain event.

For all the reasons explained above there is no doubt that hydrological and more in general environmental modelling of extended periods in Mediterranean catchments remains a challenge, particularly in wetting-up periods after the long dry summer.

2.3 Research objectives and main steps

In this work an attempt was made to identify the key hydrological and biogeochemical processes taking place in Mediterranean systems and to quantify their relative importance. Thus, the results obtained certainly could be extrapolated to progress the representation of other similar systems, if not the models themselves.

To face these issues, a progressive perceptual understanding approach, as suggested by Piñol et al., (1997) and Beven, (2001) was adopted. Namely, starting from a first basic model structure, the perceptual model was progressively modified and grown in complexity until the most characteristic processes of Mediterranean catchments were included. Finally, models assessment has been provided by means of regional sensitivity analysis.
The essential steps of this study were:

- The earlier stage of the modelling process was the understanding of the key mechanisms that should be taken into account to improve Fuirosos catchment discharge simulation. This stage concerns the perceptual model of the catchment that represents the summary of our perceptions about how it responds to the rainfall events.
- A first rainfall-runoff conceptual model (LU3) was developed to simulate the catchment hydrological response, with particular attention to represent simultaneously the dry and the transition periods as well as the wet one in a satisfactory way.
- The developed model went through a stage of parameter calibration and validation which led to a revision of the initial perceptual model of the catchment as understanding was gained from the attempt to model the hydrological behaviour. This interactive process progressively allowed including into our initial catchment perceptual model several key mechanisms to represent its behaviour. Hence, the initial lumped model structure based on three different

catchment hydrological responses (LU3) progressed to a lumped model that includes four catchment hydrological responses (LU4), and finally to a semi-distributed model structure (SD4) in which spatial variability of the evapotranspiration was considered according to the vegetation cover and to the local aspect.

- The second stage of this work focused on the catchment nitrogen dynamic simulation. In order to simulate inorganic nitrogen production and fate, a nitrogen (N) sub-model was coupled to each 4-responses rainfall-runoff models (LU4 and SD4). The initial N sub-model was based on the description of the nitrogen cycle previously proposed with the INCA model. However, the same philosophy adopted for the discharge modelling led to modify the INCA nitrogen perceptual model introducing new mechanisms as the adsorption/desorption process, nitrification and denitrification in the shallow perched aquifer and soil moisture thresholds for all the considered soil biological processes, which indeed allowed improving nitrate and ammonium simulation.
- Finally, in the third stage of this work, the developed model structures and their performances were assessed by means of General Sensitivity Analysis (Whitehead and Young, 1979 and Hornberger and Spear, 1980) and of Generalized Likelihood Uncertainty Estimation (GLUE, Beven and Binley 1992) to understand the key parameters controlling models behaviour and analyse if the additional model complexity actually gives better capability to model the hydrology and nitrogen dynamics of the Fuirosos catchment.

3

Study site

3.1 Study Site

The Fuirosos catchment (latitude 41° 42' N, longitude 2° 34', altitude range 50 - 770 m a.s.l.) is located in the northern slopes of Catalan Littoral Range, near Barcelona (Spain) and it is a tributary of the Tordera River. The catchment is an almost pristine, undisturbed forested watershed, with little agricultural activity and no urban areas. Within the catchment, there are four small reservoirs for human and cattle water supply. This water consumption can be considered insignificant during the study period. The storage volume of these reservoirs ranges from 5,000 to 18,000 m^3. The drainage area at the Fuirosos flowgauge station is approximately 13 km^2. The main rock type in the Fuirosos catchment is leucogranite (50.9%) followed by granodiorite (21.1%) and sericitic schists (23.5%) (IGME, 1983), as shown in Fig. 1. At the valley bottom there is an identifiable alluvial zone, where a well-developed riparian area flanks the Fuirosos stream channel. In this study, it was taken into account also the Grimola subcatchment, which is tributary of the Fuirosos stream draining approximately 4 km^2 (Fig. 1). In contrast to Fuirosos, Grimola does not have a significant alluvial zone. Grimola is dominated by leucogranite (70% of its area) and by sericitic schists that occupied the remaining part of the area. The catchment bedrock (mainly granite) points out that no groundwater outflows should exist at Fuirosos.

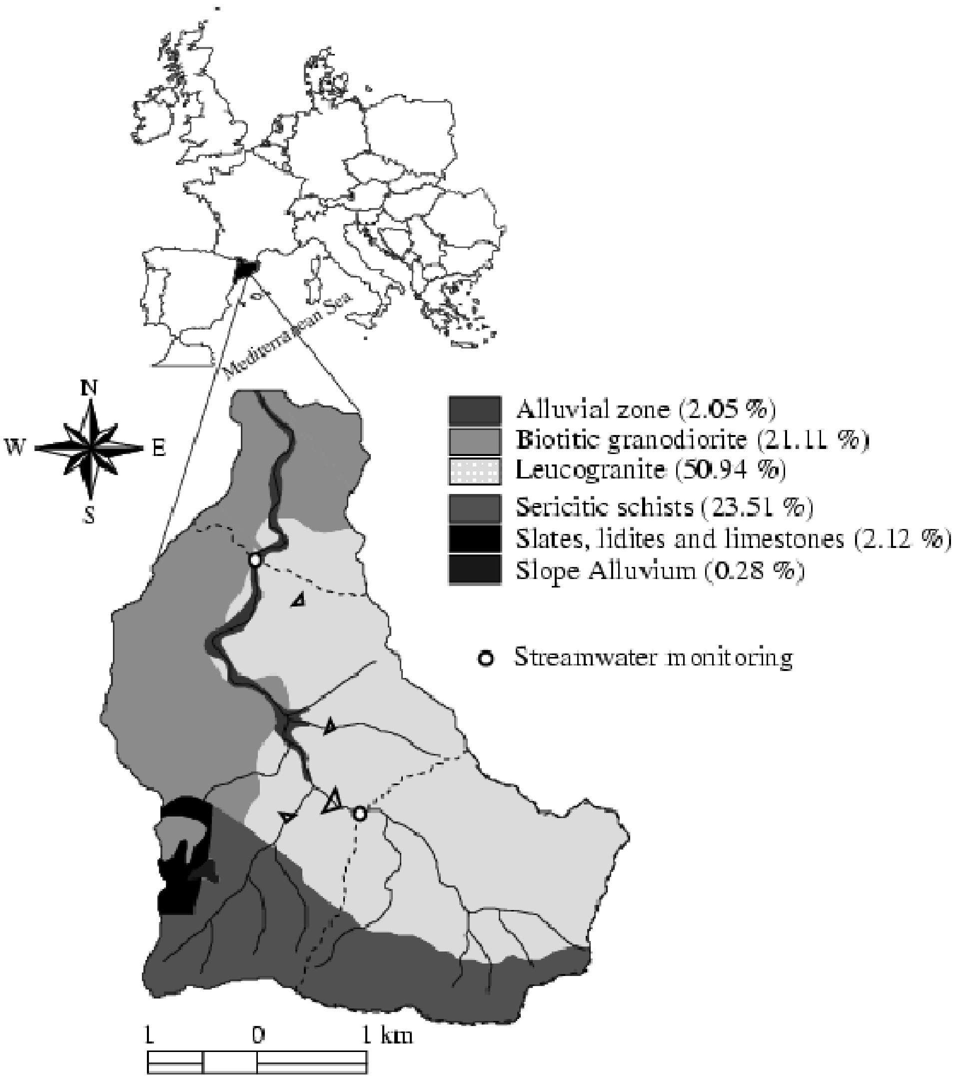


Fig. 1. Geographical location of the Fuirosos catchment and its subcatchment Grimola (Catalonia, NE Spain). Lithological units are shown in different shadings. Triangles represent the position of the four small reservoirs.

A basic fieldwork was carried out in order to study the spatial variability of certain soil physical properties. To achieve this aim, several sampling points were selected in different parts of the catchment with different bedrock types. At each one of these points an infiltration experiment was carried out with a single ring to determine relative values of surface saturated conductivity and two soil samples (at different depth) were collected. The samples were analysed to find out their texture as well as organic matter content. Results from infiltration test and laboratory analysis pointed out that the soil catchment is quite homogeneous, which is consistent with values obtained in previous studies (Sala, 1983).

The forest covers 90% of the total catchment area where perennial cork oak (*Quercus suber*) and pine tree (*Pinus halapensis* and *Pinus pinaster)* predominate. However, at the valley headwaters, mixed deciduous woodland of chestnut (*Castanea sativa*), hazel (*Corylus avellana*) and oak (*Quercus pubescens*) prevail. Sycamores (*Platanus hyspanica*) and alders (*Alnus glutinosa*) dominate at the riparian zone. Agricultural fields, grassland and urban areas occupy less than 5% of the area (Fig. 2). The observed period, at Fuirosos, is from 13/10/1999 to 30/06/2003. Original data have been published before in Bernal et al., 2004, Bernal et al., 2005, Butturini et al., 2003 and Butturini et al., 2005. Stream water level was monitored continuously using a water pressure sensor connected to a data logger. Observed mean daily stream flow at Fuirosos was obtained by an empirical rating curve achieved using a "slug" chloride addition method (Gordon, et al., 1992). At Grimola subcatchment, discharge was measured from 18/09/2000 to 22/08/2002 by a similar field station. For the period from October 1999 to December 2002, the meteorological station used was located in an open area in the valley of the Fuirosos catchment, close to the Fuirosos stream field station. The Natural Park of "*El Montnegre i el Corredor*" meteorological service (Hortsavinyà meteorological station) provided meteorological data after this period. During the complete observed period, the mean annual precipitation at Fuirosos is about 750 mm. The first hydrological year represents the driest one (annual P is about 454.2 mm) and the third one (2001/2002) the wettest (annual P is about 850.4 mm). The mean annual potential evapotranspiration (PET) computed with the Penman equation is approximately 975 mm, which is much higher than the precipitation. Therefore, the catchment must be classified as semiarid. Figure 3 shows a graph of within-year distribution of precipitation and of potential evapotranspiration at Fuirosos.

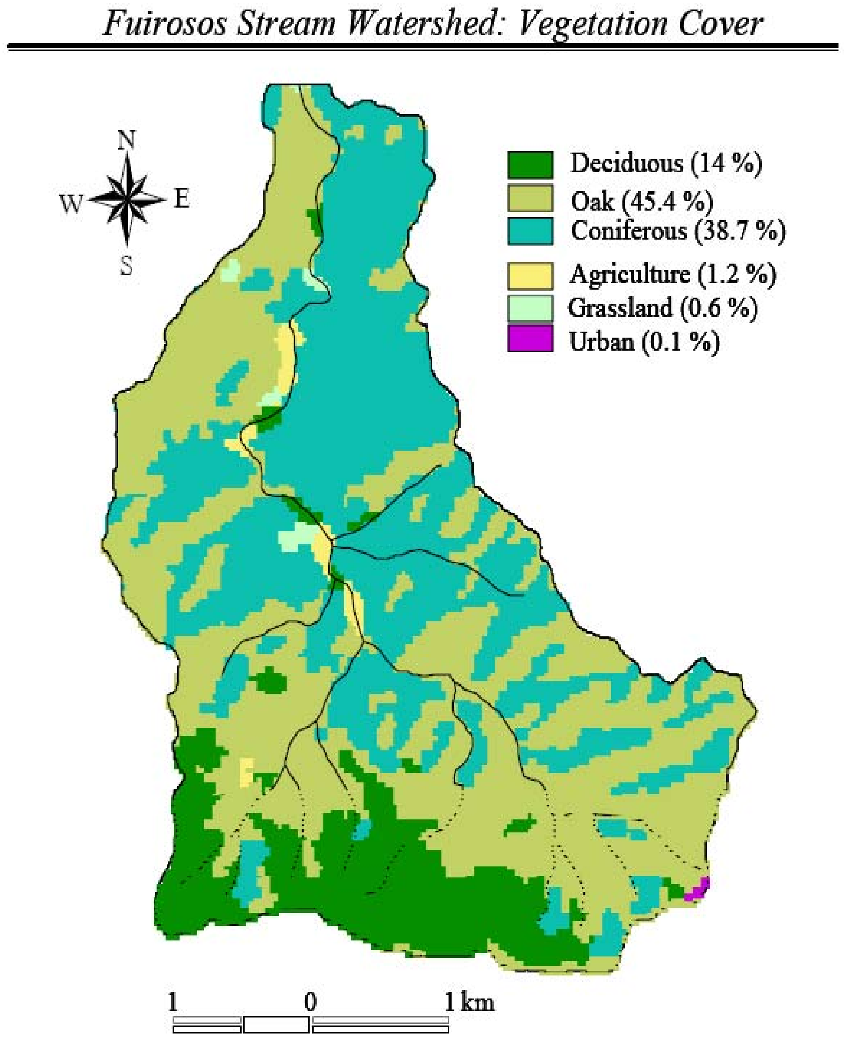


Fig. 2: Main forest types (deciduous forest, oak forest, coniferous forest) and land uses (agricultural fields, grasslands and urban areas) in the Fuirsos Stream Watershed (Catalonia, NE Spain) are shown in different colours. The area occupied by each class is shown in brackets (After Bernal 2006, PhD dissertation).

The analysis of daily precipitation enables to highlight the Mediterranean character of the climate at Fuirosos (Fig. 3). The annual average number of rainy days (P>0.4 mm) is 81, which is comparable with the number observed at other Mediterranean catchments like Vallcebre, Catalonia (91 days for year), whereas it is clearly in contrast with the number of rainy days (194 days for year) observed at Keele, a humid catchment in UK (Latron, 2003). Figure 4a shows, for the observed period 1999-2003, the monthly average number of rainy days (J_p) and the average volume per day of rain (V_p). This graph, previously proposed by Llorens (1991) (after Latron, 2003), allows to draw some conclusions about the precipitation pattern.

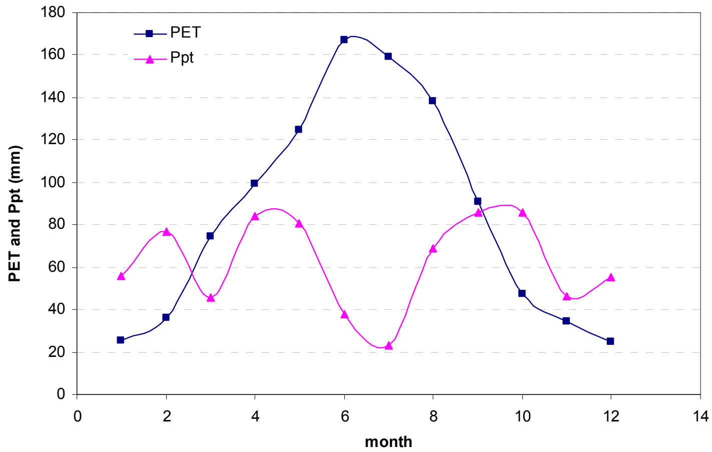
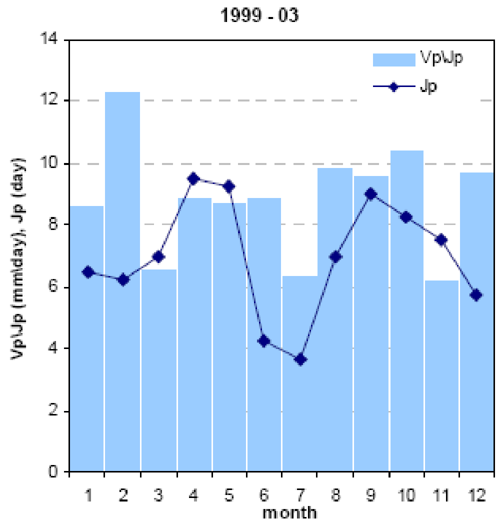


Fig. 3: Average monthly distribution of precipitation and potential evapotranspiration, computed with the Penman method at Fuirosos catchment (1999-2003).

There are two identifiable wet periods: one during spring and the other during autumn, where J_p is high, and two identifiable dry periods, summer and winter, when J_p decreases. During winter, generally, V_p is moderate, except for February when the highest value of V_p/J_p is observed. This is due to an extraordinary monthly precipitation occurred in February 2003 (Fig. 4b). Generally, during spring, the value of $V_p\backslash J_p$ is similar to the one observed in winter (apart from February), even though J_p increases considerably, hence indicating the presence in this season of a greater number of days with small to moderate precipitation. On the other hand, during summer J_p decreases, but due to characteristic convective storms, the value of $V_p \backslash J_p$ increases (August). Finally, during autumn $V_p \backslash J_p$ reaches its maximum value (without considering February) due to large rainfall events (frontal storms).

a.



b.

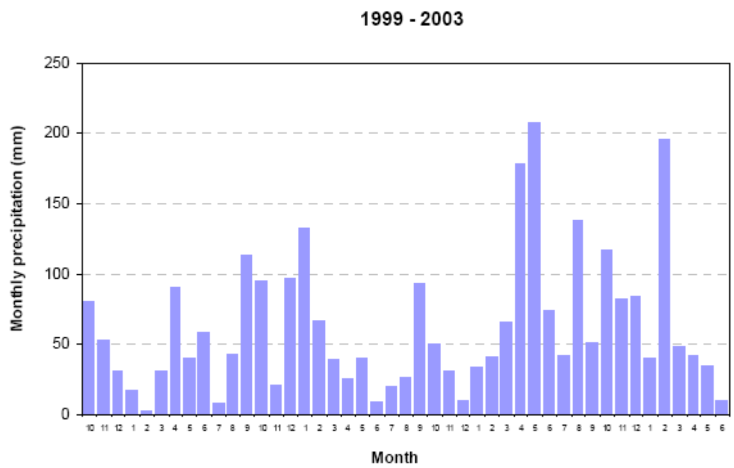


Fig. 4: a) Average number of rainy days for month (J_p) and volume of rain per rainy day (V_p/J_p) at Fuirosos (1999-2003). b) Monthly precipitation during the observed period at Fuirosos catchment.

The calculated annual runoff deficit (D) (precipitation P less runoff Q) for the Fuirosos catchment is approximately 640 mm, with a coefficient Q/P of 15%, which is in the range of values calculated for Mediterranean catchments. Considering an annual balance of water, it could be said that the runoff deficit is basically related with the actual evapotranspiration from catchments, if there is no evidence of groundwater outflow. Figure 5 shows the relation between precipitation and runoff deficit for a period of twelve consecutive months.

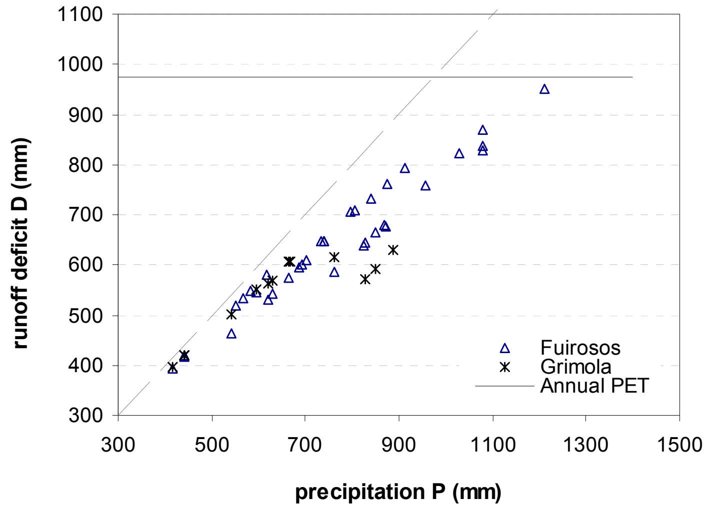


Fig. 5: Relation between precipitation and the runoff deficit for twelve consecutive months for both the Fuirosos and Grimola streams. Values have been obtained by a mobile sum over twelve months of the available values. This procedure has previously been adopted by Latron (2003).

Figure 5 points out a peculiar behaviour of both Fuirosos catchment and its subcatchment Grimola, since the runoff deficit gradually increases with precipitation. This behaviour contrasts with the normal tendency observed (Piñol, 1999, Latron 2003). Also Latron (2003), in his research at Vallcebre, found the same behaviour at two of the four subcatchments studied and concluded that such pattern could be explained by groundwater losses due to the presence of an extended limestone layer. In this case, the

percentage of the total area constituted by limestone (Fig. 1) is too small to justify entirely this behaviour and on the other hand, the granitoid bedrock is thought to be almost impermeable.
Another interesting analysis is the one called “ordered runoffs”, with which it is possible to compare the hydrological response of the Fuirosos catchment and its subcatchment Grimola (Fig. 6). This representation consists in ordering the observed daily runoffs from the greater to the smaller one, without taking into account their temporal succession (Castany, 1996, after Latron 2003).

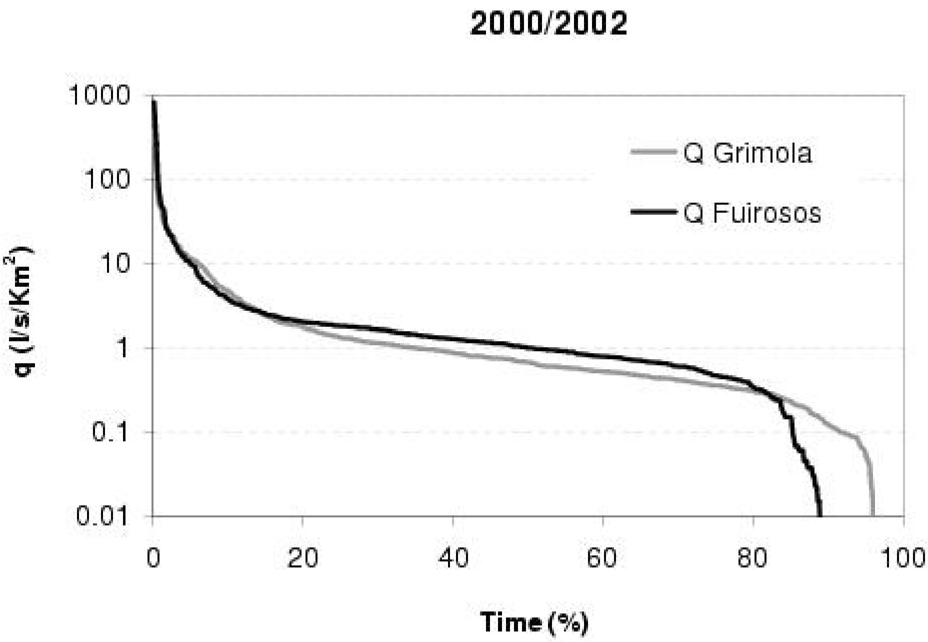


Fig. 6: Specific daily stream discharge ordered from the highest to the lowest for the Fuirosos catchment and the Grimola subcatchment from 18/09/2000 to 22/08/2002 (Observed data provided by the Universitat de Barcelona, Departament d’Ecologia).

From Figure 6, it can be noticed that the Fuirosos catchment shows a clear tendency to get dry easier then the Grimola subcatchment, during low flow. This behaviour could be explained considering the presence of a well-developed riparian area at the valley bottom of the Fuirosos catchment overlapping the alluvial zone.

Concerning the catchment hydrochemical characterization, daily streamwater nitrate (NO_3) concentrations were also measured in water samples taken from the catchment outlet during the period from October 1999 to April 2003 and daily ammonium (NH_4) concentrations were also measured during the period from January 2001 to August 2002. Baseflow stream water samples were taken at least once every ten days. To monitor nutrient dynamics during stormflow, the automatic sampler was programmed to start sampling at an increment in the streamwater level of 2-3 cm. In this way water samples were taken during the rising and the recession limb of the hydrograph. A daily average of nitrogen concentrations during stormflow conditions was used to compare simulated and measured daily nitrogen concentration. Figure 7 summarises nitrate and ammonium variation ranges during both baseflow and stormflow conditions and splitting the data into three different seasons: the transition period (form September to November), the wet period (from December to February) and the so called ‘vegetation period’ (from March to May). It was observed that in general nitrate was consistently low during from September to November and from March to May, while it tends to increase during the wet season. On the other hand, ammonium concentrations were higher after the drought than during the wet season. For a detailed description of the Fuirosos chemical water analyses see Bernal et al. (2004; 2005).

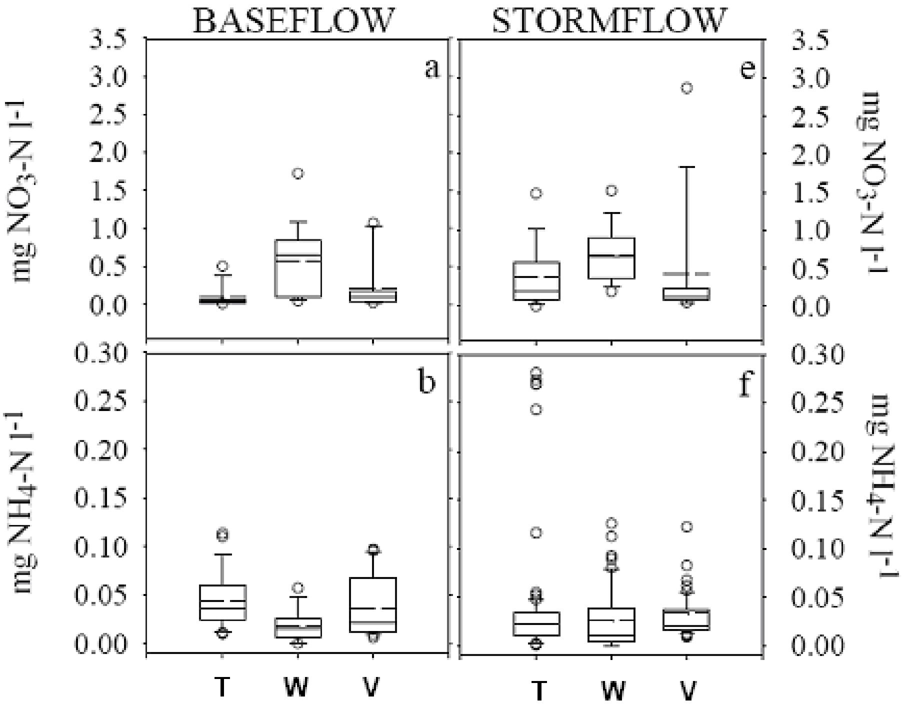


Fig. 7: Box plots summarising concentration data (mg l-1) in streamwater at Fuirosos (Catalonia) during baseflow (left panles) and stormflow (right panels) conditions. The centre horizontal line in each box is the median value of concentration, The dashed line is the mean concentration. Fifty percent of the data points lie within each box. The whiskers above and below the box indicate the 90% and the 10% percentiles. Circles are outliers. T: transition period; W: wet period; V: vegetative period (After Bernal et al., 2005)

4

Papers

4.1

*Modelling the non-linear hydrological behaviour of a small Mediterranean forested catchment**

Key words

Perceptual modelling; Mediterranean intermittent stream; riparian zone

*C. Medici, A. Butturini, S. Bernal, E. Vázquez, F. Sabater, J. I. Vélez, F. Francés. 2008. Hydrological Processes 22: 3814-3828.

1. Introduction

Catchments under relatively dry climate are characterised by strong non-linearities in their hydrological behaviour (Ye et al., 1998, Piñol et al., 1999). Consequently, reproducing their complex non-linear behaviour presents a great challenge to rainfall-runoff modelling. This is especially true for Mediterranean regions, which share the hydrological processes from both wet and dry environments, following a seasonal pattern that induces remarkable particularities in their hydrological behaviour (Gallart et al., 2002).

It is well known that the hydrological response to a storm is greatly dependent on the soil water initial state, which for a Mediterranean catchment is highly variable because of the large range of weather conditions. This fact leads in Mediterranean catchments to complex stream hydrology, characterized by a high annual variability of the water balance. To this end, several authors have pointed out three recognizable periods during a hydrological year (Piñol et al., 1997; Gallart et al., 2002; Latron 2003): a long dry season; a wetting-up period (during which large rainfall events may produce little or no response at the flow gauge station); and finally a wet season.

In particular, the wetting-up period is a critical point for the hydrological and hydrochemical functioning of Mediterranean catchments (Durand et al., 1993) and generally, rainfall-runoff models cannot reasonably reproduce the shape of the associated hydrographs (Piñol et al., 1997; Anderton et al., 2002; Latron et al., 2003; Bernal et al., 2004). Some authors (Burch et al., 1987; Gaillard et al., 1995; Taha et al., 1997; Beven, 2002a) have emphasized the appearance, during the wetting-up period, of a perched water table at the interface between a higher permeable layer and a lower one and how subsurface flow is rapidly generated by this perched saturated level. Moreover, Ocampo (2006) found that shallow subsurface flow (continuous or not) in an intermittent stream can occur in transient local flow regimes, particularly in small headwater forested and agricultural catchments. Its development depends upon the rainfall and/or snowmelt regime, unsaturated soil thickness, permeability, and the presence of an impeding layer (bedrock or clay).

It has been pointed out that during the dry period there may be a disconnection of the permanently saturated zone from the stream network system. To this end, Grayson et al. (1997) and Gallart et al. (2002) suggest a “switching” behaviour of the underground water transfer due to the lowering of the water table. In addition, Marc et al. (2001) remarked in their work that the saturated zone is likely to be constituted of a deep aquifer and it did not contribute to the discharge during the study period at a small Mediterranean forested catchment. It is only during the wet period when all the system becomes completely integrated.

Less attention has been paid to the potential influence that the riparian zone can have on the observed hydrograph, especially during the drying-up and the wetting-up periods. Tabacchi et al. (2000) pointed out that vegetation could have a significant impact on hydraulic processes, particularly during periods of low flow. Others authors affirmed that riparian vegetation consumes groundwater and streamwater (Chen, 2006) and have suggested that, in summer, the riparian water table may fall significantly; so, under these conditions, the normal hydraulic gradient may reverse, with discharge from the river to the riparian zone (Burt et al., 2002; Butturini et al., 2003). In the analysis of an intermittent stream, this may represent an important mechanism to take into account in order to explain its non-linear behaviour. Moreover, McMahon (2005), analyzing several Australian catchments, has postulated that the hydrograph steep recession is a combination of evaporation from the stream surface and transpiration of the riparian vegetation, which together are greater than the recharge to the stream by local groundwater.

Concepts and ideas developed by modellers for humid climate usually fail when applied to semi-arid regions and lead in many cases to unsatisfactory results. That was the case of the semidistributed INCA model (Wade et al., 2002) when applied to a small Mediterranean catchment, Fuirosos, drained by an intermittent stream (Bernal et al., 2004) and which is also the case study in this paper. Bernal et al. (2004) showed that with only one set of parameters, INCA was not able to capture the characteristic inter-annual and intra-annual variability of the Fuirosos catchment. A better simulation of the hydrology in semiarid systems is not only an academic interest. On the contrary, it represents a key issue to asses the hydrological management of these critical areas (Chiew et al., 2002) and to achieve a good prediction of geochemical and ecological responses (Schlesinger et al., 2006). The challenge of our study was to improve the representation and understanding of the hydrological processes in Mediterranean catchments, with special attention to the key factors that govern the drying-up and the wetting-up periods such as soil moisture, the existence of a perched water table and the potential effect of the riparian zone. To face these issues, a progressive perceptual understanding approach (Piñol et al., 1997; Beven, 2001) was adopted to better reproduce the observed hydrograph at Fuirosos. I.e., starting from a first basic model structure, the perceptual model was progressively modified and grown in complexity until the most characteristic hydrological processes of Mediterranean catchments described above were included.

2. Model evolution and results of the calibration process

We generally learn most when a model or theory is shown to be in conflict with reliable data so that some modification of the understanding on which the model is based must be sought (Beven, 2000, page 1)

This sentence synthesizes the fundamental idea and practical approach adopted in this research. During this work, the earliest perception of how the Fuirosos catchment responds to a rainfall episode progressively changed and, therefore, it changed the related conceptual model. In the next sections four different model structures are described, each one of them with the corresponding calibration results. These four conceptualizations represent the fundamental steps of the perceptual catchment model evolution, saving to the reader the complete sequence of tested model structures. These conceptual models try to represent the hydrological processes at catchment scale, rather than at the point scale. A daily time step was adopted for the simulations.

The calibration period was the same considered for the INCA model calibration (Bernal *et al*. 2004) and covers approximately three hydrological years (from the 13th of October 1999 to the 22nd of August 2002). This period was chosen also because it presents highly contrasting hydrological conditions that are necessary to capture all the particularities of the hydrological catchment behaviour.

Parameters were optimized taking into account the Nash and Sutcliffe efficiency index E (Nash, J. E. and J. V. Sutcliffe, 1970), the balance error in terms of observed and simulated global volume, BE, and the graphical fit between observed and simulated hydrographs. The global BE was split into partial BE associated to four different discharge ranges in order to understand and compare the blind spots of the different model structures. The first discharge range concerns the “extremely dry” period, including the last days of the drying-up sequence and the first days of the wetting-up sequence ($Q < 0.005\ m^3/s$). The second one represents the “base flow” range ($0.005\ m^3/s \leq Q < 0.05\ m^3/s$). The third range corresponds to the “intermediate” flow ($0.05\ m^3/s \leq Q < 1\ m^3/s$) and finally the last one includes the “flood” discharge ($Q \geq 1\ m^3/s$). The observed and simulated maximum peaks and the number of days associated to a very low discharge ($Q < 0.001\ m^3/s$) were also considered to evaluate the models performances.

The adopted calibration procedure started with a preliminarily automatic calibration using the “solver” command in MS Office Excel 2003. Search bounds for each parameter were fixed a priori, taking into account its physical meaning, the field observations and/or previous experience. The aim of this step was to achieve the best E index, without considering the general shape of the hydrograph. A basic sensitivity analysis was performed by varying each parameter, individually, from its calibration value. After that, a systematic manual correction of the more sensitive parameters was carried out focusing on the graphical fit and some specific parts of the hydrograph (e.g., recession curves, levels of baseflow, as well as the peaks).

The parameters involved in each model structure and their values after the calibration process are described in Table 1. The goodness indexes for each model are summarized in Tables 2 to 4. From a modelling point of view, these calibrated parameter values have to be understood as “effective” values (Francés et al., 2007). Mertens et al. (2005) pointed out that, in general, optimized or “effective” parameters do not correspond to the ones estimated in the laboratory or *in situ*. These differences are due to several reasons such as temporal and spatial scaling effects and/or model and input errors (Mertens et al., 2005; Francés et al., 2007). Therefore, the conceptual model of a system and its parameters may not be realistic or completely consistent with the perceptual model in itself, though it can be used to produce quantitative predictions within the limits of its own definition (Beven 2002b).

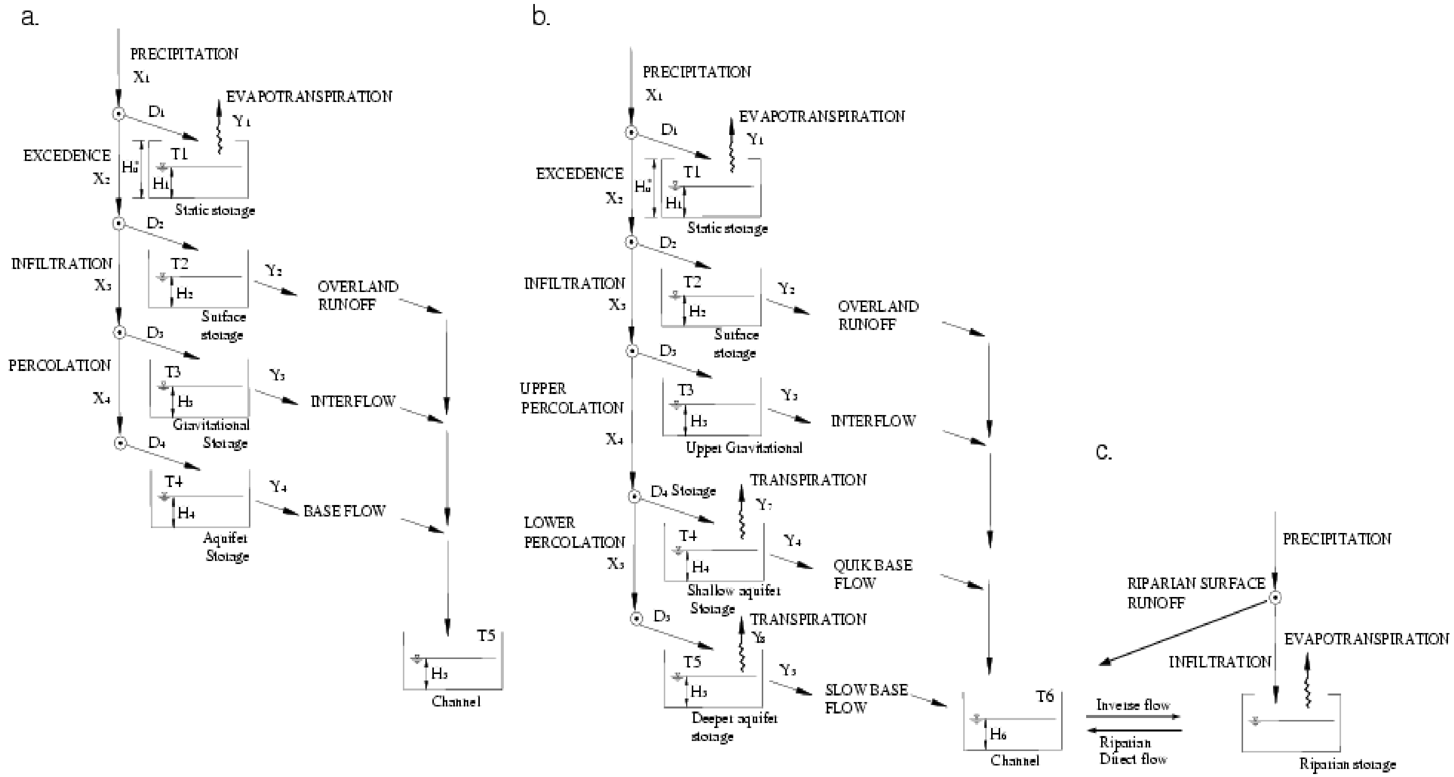


Fig. 3. Schematic representation of a) the LU3 model structure; b) the LU4 model structure, which also has been used for the semidistributed structure at each HRU; c) the riparian tank added to the SD4 model structure to obtain the SD4-R.

3. First Conceptualization: 3-response lumped model (LU3)

3.1 LU3 model description

The starting point for the modelling of the Fuirosos catchment was a lumped version of an already existent distributed conceptual model, called TETIS (Francés et al., 2002 and 2007). It consists of a series of connected tanks, each one representing different water storages in the soil column: static (interception, water detention in puddles and retained water by upper soil capillary forces), surface, gravitational (upper soil water content above field capacity) and aquifer. The vertical connections between tanks describe the precipitation, evapotranspiration, infiltration and percolation processes. The horizontal flows describe the three different responses: the overland runoff, interflow and a base flow (Fig. 3a). The *overland flow* is associated with water flowing over the surface or into the organic horizon (horizon O) and it is computed following a Hortonian mechanism. This flow is not expected to appear frequently, since the soil infiltration capacity at Fuirosos is generally high. The production of overland flow due to the saturation of the soil has not been taken into account, since it is thought that the soil is hardly ever saturated in Fuirosos. The *interflow* is the response that at Fuirosos occurs into the soil-gravel layer (horizon A), with a lower propagation velocity than the overland flow. Finally, the *base flow* is the response from the aquifer or permanently saturated zone.

Firstly, the model computes the amount of water intercepted by plants, detained in puddles and hold into the upper soil by capillary forces.

This water fills the static tank of the model according to an equation already used by the HBV model (Bergström, 1995) and the GR-3j model (Arnaud and Lavabre, 1996):

$$D_1(t) = \min\left\{ X_1(t) \cdot \left(1 - \frac{H_1(t)}{H_u^*}\right)^2 ; H_u^* - H_1(t) \right\} \tag{1}$$

where: $D_1(t)$ is the water entering into the static storage (mm/day); X_1 is the daily precipitation (mm/day); H_1 is the actual static storage water content (mm); H_u^* is the maximum static storage water content (mm) and t is the time step (day).

Water can leave the static tank only by evapotranspiration, which is computed in a simple way, as follows:

$$Y_1(t) = min\{ET_0(t) \cdot FC ; H_1(t)\} \tag{2}$$

where: $Y_1(t)$ is the actual daily evapotranspiration from the static storage (mm/day); ET_0 is the reference daily evapotranspiration for the catchment (mm/day) which in this case has been considered the same that the potential evapotranspiration (PET) and FC is its correction factor. Water not retained is free to move and supplies the other three tanks (surface, gravitational and aquifer). They act as linear storages characterized by different residence times. The model philosophy is that water moves downwards whenever the outflow capacity of each tank (K_s and K_p) is not exceeded.

Table 1. Parameters considered in each of the four model structures (LU3, LU4, SD4, and SD4-R) and their effective values after the calibration process.

			LU3	**LU4**		**SD4**			**SD4-R**		
Param.	Units	Descript.			Leuco.	Grano.	Sch.	Leuco.	Grano.	Sch.	R. Zone
Thresholds											
H_u^*	mm	*Maximum static storage water content.*	180	175	150	150	150	150	150	150	----
$H_{r\text{-}max}$	mm	*Maximum water storage capacity of the riparian storage*	----	----	----	----	----	----	----	----	1785
H_m	mm	*Threshold water content of T1 for deep percolation*	----	100	50	90	90	50	90	90	----
Maximum flow capacities											
K_s	mm d^{-1}	*Surface infiltration capacity*	20	25	25	25	25	25	25	25	----
K_p	mm d^{-1}	*Percolation capacity of horizon B*	2	6	12	12	12	12	12	12	----
K_{pp}	mm d^{-1}	*Percolation capacity to weathered bedrock aquifer*	----	5	12	12	11	12	12	11	----
K_r	mm d^{-1}	*Riparian infiltration capacity*	----	----		----					20
Water residence times											
t_1	days	*Surface storage*	1	1	1	1	1	1	1	1	----
t_2	days	*Upper gravitational storage.*	2	2	1.73	2.30	1.73	1.73	2.30	1.73	----
t_3	days	*Lower gravitational storage.*	22	22	25	25	25	25	25	25	----
t_4	days	*Weathered bedrock aquifer storage.*	----	3000	3000	3000	3000	3000	3000	3000	----
FC	Ø	*Correction factor for the PET.*	0.9	0.9		0.9			0.9		1
ά	Ø	*Discharge coefficient for the channel storage*	----	----		0.95			0.95		

The continuous water balance allows obtaining a better estimation of the antecedent moisture condition before the storm event, which has a great importance especially for Mediterranean regions. The LU3 model presents six parameters to be calibrated plus one correction factor (FC) used for the computation of the PET in order to take into account the associated uncertainty, as it is shown in Table 1.

Table 2. Calibration efficiency indexes (from 13/10/1999 to 22/08/2002): the Nash index (E); the global and partial balance volume errors (BE); the simulated maximum peak of discharge (Sim. Q)[a]; the simulated number of days with Q < 0.001 m3/s (Sim. N.)[b]

Model structure	E	Sim. Q m^3/s	Global BE %	Partial BE % $Q < 0.005$ m^3/s	Partial BE % $0.005 \leq Q < 0.05$ m^3/s	Partial BE % $0.05 \leq Q < 1$ m^3/s	Partial BE % $Q \geq 1$ m^3/s	Sim. N. m^3/s
LU3	0.71	6.7	47.4	1.8	25.6	38.4	-18.4	147
LU4	0.72	6.3	-1.3	1.3	6.9	12.6	-22.2	248
SD4	0.77	8.6	1.2	2.2	2.7	13.0	-16.8	92
SD4-R	0.78	8.6	-1.0	1.1	2.1	12.6	-16.8	212

[a] The observed maximum peak is 10.9 m^3/s.
[b] The observed number of days with $Q < 0.001$ m^3/s is 220 days.

3.2 LU3 model results and discussion

Observed daily stream flows at Fuirosos and the corresponding simulated ones obtained with the LU3 model structure are shown in Fig. 4a. The sensitivity analysis pointed out that H_u^* was the parameter that affected the most the simulated total flow, which increased by 38% when H_u^* was reduced by half. In contrast, the same change in any of the other parameters affected total simulated flow by less than 1%. Despite E was relatively good (0.7), the model could not reproduce reasonably well the observed hydrograph shape. In particular, the model presented two major blind spots: one was the global BE that was around 50% (which means that the LU3 model largely overestimates the observed discharge) and the other one concerned the poor simulation of the stream drying-up and wetting-up (Table 2). The analysis of the partial BE and of the graphical fit pointed out that neither the LU3 model was able to reproduce satisfactorily the base flow nor the intermediate flow. It can be also noticed that the greatest simulated peak flow (6.7 m^3/s) was quite low compared with the observed one (10.9 m^3/s), though the observed value is illustrative because the storm event was so severe that the field equipment was swept away by the flood (personal observation).

The high BE suggested that a key process involved in the Fuirosos water balance was lacking in its conceptualization. Since groundwater outflow was not acceptable in Fuirosos, evapotranspiration was the most likely candidate.

It was also observed that during the wet period the simulated recession did not fit well the observed one, since the LU3 model clearly overestimated the related base flow. On the other hand, the LU3 model was able to capture the recession curve during the wetting-up period. This result suggested that water flow paths were not equivalent during these two periods. Therefore, other non-linear mechanisms should be considered in order to explain this behaviour.

4. Second Conceptualization: 4-response lumped model (LU4)

4.1 LU4 model description

The LU4 model based its structure on the LU3 model, but it splits the aquifer storage in two tanks that generate different water recession curves due to different drainage rates, as it is done by the classical Sacramento SMA model (Peck, 1976). The new model structure involves four different catchment hydrological responses (Fig. 3b). The *quick base flow* represents the flow that occurs into the upper part of the weathered bedrock (horizon B) due to the formation of a perched *shallow aquifer*. The *slow base flow* considered in this study is associated with the permanently saturated zone within the deeper weathered bedrock layer (called *deep aquifer* in this paper). This new four-response structure is coherent with results obtained in previous field works at Fuirosos. In fact, Butturini et al. (2003) estimated that in the Fuirosos riparian zone there was a weathered granite layer (WBR), a sandy-gravel soil layer (SG), and a surface organic soil layer poorly developed overlying the bedrock. The saturated conductivity values in the SG layer ranged between 12 m/day and 19 m/day, meanwhile the upper part of the underlying WBR layer averaged 4.8 ± 3.12 m/day and, finally, the hydraulic conductivities of the deeper WBR layer averaged $9.6 \cdot 10^{-3} \pm 3.7 \cdot 10^{-3}$ m/day. Even though these results refer to a limited study area, they agree with the general description made by Maréchal et al. (2006) of a weathering profile of a granite aquifer in which the density of fissures decreases with depth and so does the hydraulic conductivity.

Percolation to the deep aquifer occurs only when soil water content exceeds a threshold value. Only during the wet season, when water table level raises due to large rainfall events, may the permanently saturated zone (deep aquifer) be connected to the stream. A threshold value of the static storage is also considered in the ModSpa model (Moussa et al., 2007) to compute infiltration and percolation processes in a Mediterranean mountainous catchment.

Therefore, percolation in Fig. 3b was computed as follows:

If H_1 (t) ≥ H_m :

$$X_4 = X_1 - D_1 - D_2 - D_3 = D_4 + X_5 \quad (3)$$

$$D_4(t) = max\{X_1(t) - D_1(t) - D_2(t) - D_3(t) - K_{pp}; 0\} \quad (4)$$

$$X_5 = X_4 - D_4 \quad (5)$$

If H_1 (t) < H_m :

$$X_4 = X_1 - D_1 - D_2 - D_3 = D_4 \;; \qquad X_5 = 0 \quad (6)$$

$$D_4(t) = \max\{X_1(t) - D_1(t) - D_2(t) - D_3(t); 0\} \quad (7)$$

where: X_4 is the water that percolates to the aquifers (mm/day); D_2(t) is the water that enters into the surface storage (mm/day); D_3(t) is the water that enters into the gravitational storage (mm/day); D_4(t) is the water entering into the shallow aquifer (mm/day); X_5 is the water percolate to the deeper aquifer (mm/day); K_{pp} represents the maximum amount of water that can percolate to the deep aquifer at each time step (mm/day) and H_m is a threshold value of the static storage (mm) for deep percolation.

In order to reduce the overestimation of stream runoff simulated by the LU3 model (global BE = 47.4%), the LU4 model accounted for the transpiration from both the shallow and the deep aquifers, assuming that vegetation would be able to extract water from this compartment by its deep root system. The transpiration from these two tanks completes the deficit between the PET and evapotranspiration from the static tank, if there is enough water available. The actual evapotranspiration was computed sequentially, starting from the static tank, then the shallow aquifer tank and finally the deep aquifer tank.

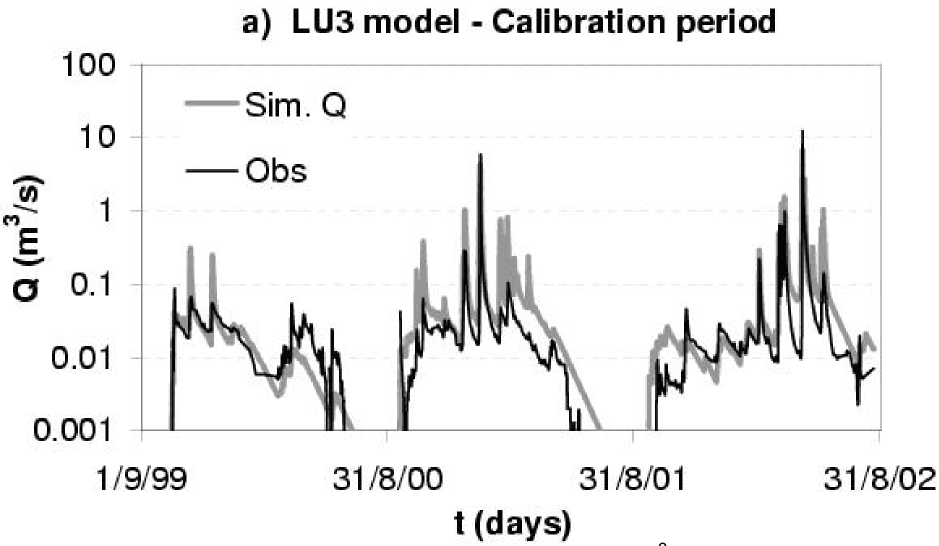


Fig. 4a. Observed and simulated daily discharge (m^3/s) during the calibration period, from 13/10/1999 to 22/08/2002, obtained by the LU3 model

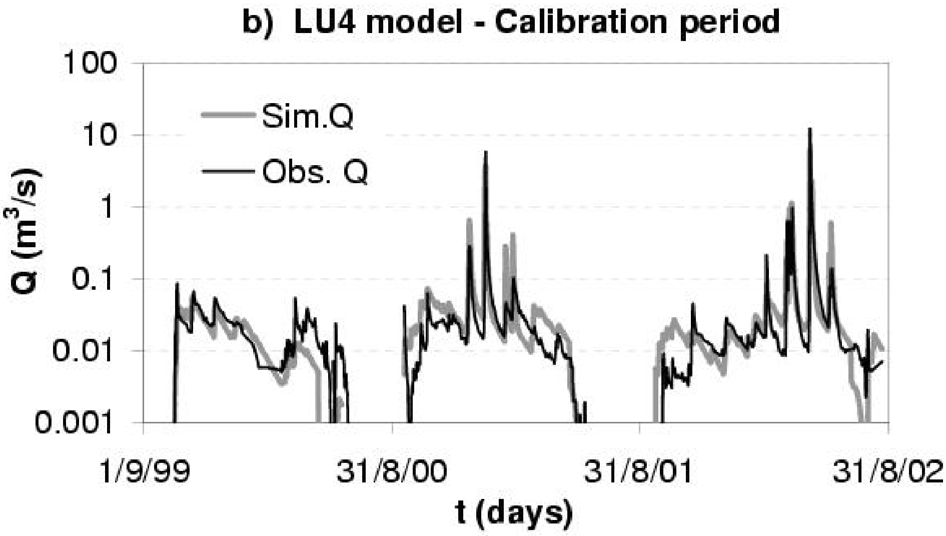


Fig. 4b. Observed and simulated daily discharge (m^3/s) during the calibration period, from 13/10/1999 to 22/08/2002, obtained by the LU4 model

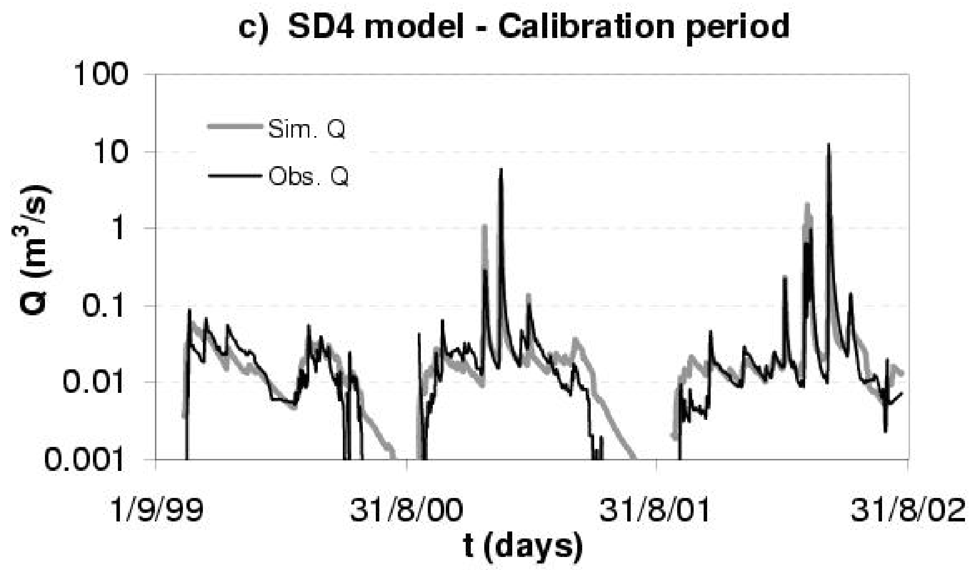


Fig. 4c. Observed and simulated daily discharge (m^3/s) during the calibration period, from 13/10/1999 to 22/08/2002, obtained by the SD4 model

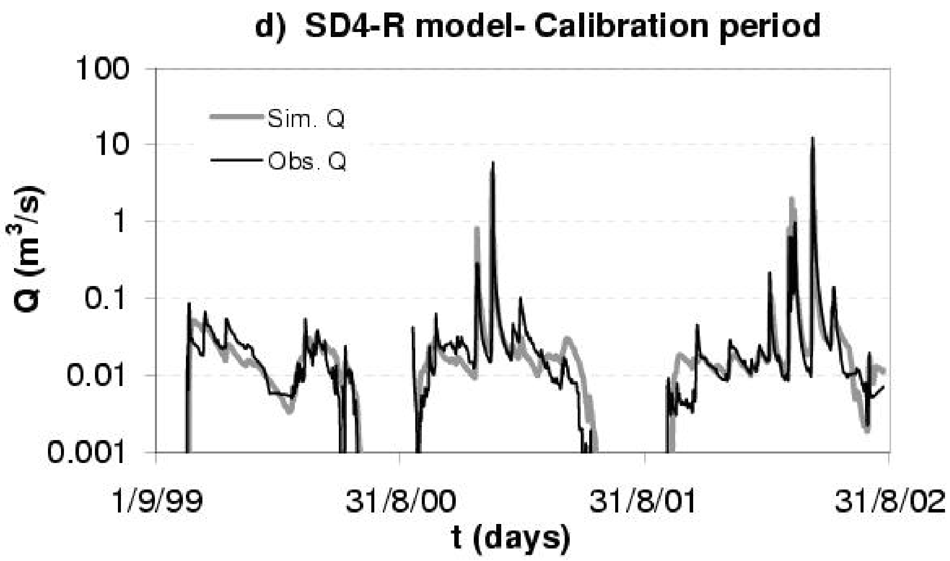


Fig. 4d. Observed and simulated daily discharge (m^3/s) during the calibration period, from 13/10/1999 to 22/08/2002, obtained by the SD4-R model

4.2 LU4 model results and discussion

The LU4 model structure was based on a total of nine parameters plus the correction factor FC for the PET that has been left as in the LU3 model (Table 1). Similarly to the LU3 model, the sensitivity analysis pointed out that the total flow was mostly influenced by the parameter H_u. A reduction of H_u by 50% increased total flow by 102% while changing by ±50% any of the other parameters affected total simulated flow by less than 30% (e.g., the reduction of H_m affected the total flow by -27%, while the reduction of K_{pp} by 19%). Observed daily stream flows at Fuirosos and the corresponding simulated ones obtained with the LU4 model structure can be seen in Fig. 4 b. The index E (0.72) did not improve much compared with the LU3 one, since the greatest peak flow simulated (6.3 m^3/s) was still lower than the observed one. In any case, according to our analysis following the assumptions of McCuen et al. (2006), it could be considered significantly different from the LU3 efficiency index E, since its value was extremely closed to the 95% upper confidence limit (0.7293). Moreover, the global BE was reduced to only -1.3% (Table 2). Overall, the partial BE analysis pointed out that the greatest improvement obtained with the LU4 model concerns the base flow and intermediate flow simulation. This is mainly due to the new groundwater conceptualization. The deep aquifer represents the permanently saturated zone, which is thought to be constituted by several bedrock depressions that may exert a significant control on water mobility (McGlynn et al., 2002). This high water residence time led to loose more water by transpiration than by base flow from this storage. The recharge to this permanently saturated zone, according to the non-linear percolation of the LU4 model conceptualization, occurred mainly during the wet period and the corresponding water was stored into it until the build-up of the saturation. On the other hand, during dry conditions, the water could not percolate to the deep aquifer, but it accumulated into the upper weathered bedrock layer forming a transient saturated area (characterized by a lower water residence time) from which the quick base flow was generated. This mechanism is thought to be the key process during the wetting-up. In concordance with our results, Bernal et al. (2004) also pointed out that the major difference among the calibrated INCA parameters, between dry and wet years, was the residence time of water in the groundwater compartment.

These hypotheses are also supported by previous researches carried out by several authors. For example, Pilgrim et al. (1988) and Ye et al. (1998) pointed out that in arid and semiarid regions the permanent water table is typically below streambed and disconnected from the surface drainage system, even though a temporary saturated hydraulic connection may occur during flood events. They also affirmed that most rainfall events in arid and semiarid regions involve relatively small rainfall depth; hence, it is likely that significant recharge of this saturated areas from general infiltration occurs only in extreme events, which agrees with the LU4 model conceptualization.

The introduction of a threshold value (H_m) controlling when percolation to the deep aquifer occurs in the LU4 model was fundamental to achieve a good fit. If such a threshold was not included (that is, if water would always percolate to the deep aquifer, regardless of soil water content), the global BE would be about -30%. This would lead to a lack of discharge during dry conditions and thus, to a bad simulation of the driest year and the wetting-up periods. In fact, Bernal et al. (2004) found that the INCA model index determining water percolation from soil to groundwater was lower during dry than during wet years at the Fuirosos catchments. To this end, Butterworth et al. (1999) pointed out that in dryland environments deep drainage or groundwater recharge often not occur at all during poor rainfall years, when the surface redistribution of rainfall is more difficult, while in wetter years groundwater recharge is more likely to occur at all locations.

Water depleted from the saturated zone (shallow and deep aquifers) as transpiration can be associated to the mechanism called hydraulic lift. The temporary stored water to the upper soil layer around the plant is thought to be rapidly absorbed by the vegetation, so is not added to the static tank, but directly release to the atmosphere, as in the Sacramento SMA model. As pointed out by Caldwell et al. (1998), the amount of water moved by hydraulic lift may contribute significantly to the actual evapotranspiration, especially in arid and semiarid environments, and the importance of deep roots in the water balance of ecosystems is receiving increased interest (e.g. Canadell et al., 1996). In the present study, the contribution from the saturated zone to the total transpiration calculated by the LU4 model was 9.1% and 0.2% of the mean annual evapotranspiration, for the deep and shallow aquifers respectively. The static tank accounted for the remaining part. The relative importance of the shallow aquifer transpiration in reducing the global BE was small, but it was relevant for reproducing the drying-up period. In fact, the number of days with a simulated discharge less than 0.001 m^3/s decreased from 258 to 151 when the transpiration from the shallow aquifer was not considered.

Despite these good results, the LU4 model was still not able to satisfactorily simulate the first dry year and the non-linear response observed during the first autumnal storm, advancing the starting moment of the wetting-up period (Fig. 4b). Also the potential effect of the small reservoirs was not explicitly included, which can be important during the drying-up of the catchment because the reservoirs seepage may last until summer.

5. Third Conceptualization: 4-response semidistributed model (SD4)

5.1 SD4 model description

The SD4 model represents the semidistributed version of the LU4 model. Three main lithological units were considered: leucogranite with eastern orientation slopes, granodiorite with a western orientation and sericitic schist with a northern orientation (Section 2, Fig. 1). In addition, five subcatchments were defined, four of which drain to the small reservoirs present at the catchment, while the fifth one represents the rest of the catchment. The intersection of the three lithological units and the five subcatchments gave rise to eight hydrological representative units (HRUs). The LU4 model has been applied to every HRU, so each one of them was still described by a set of nine parameters. The differences between the parameter sets only depend on the lithology (Table 1), which means, for example, that all the HRU overlying leucogranite were characterized by the same parameter values.

The stream was described as a linear tank, which receives directly the contribution of all the HRUs and it was characterized by a discharge coefficient (α) to be calibrated. In addition, the effect of the four small reservoirs on the catchment response was included into the model. Depletion of water from the reservoirs may occurs by evaporation, by dam seepages (linearly dependent with the actual stored volume), and/or by overflow when the reservoir maximum capacity is exceeded. In case of overflow, it was checked that flood routing was not significant at daily scale. The reservoirs parameters were estimated and not calibrated.

Another additional feature introduced in the model for the evapotranspiration computation was the consideration of the spatial variability of the PET. In the case of the actual evapotranspiration from the static tank is now computed as follows:

$$Y_1(t) = min\{\lambda(m) \cdot \beta(m) \cdot ET_0(t) \cdot FC; H_1(t)\} \tag{8}$$

where $\lambda(m)_{m=1,12}$ is a non-dimensional monthly index that takes into account the vegetation cover temporal variation. Each lithological unit has a different set of $\lambda(m)_{m=1,12}$ according to its representative vegetation (deciduous or perennial). On the other hand, β(m) is the aspect index, which takes into account the potential sunshine arriving to each lithological unit according to its representative aspect and surrounding relief (Pardo et al., 1999).

5.2 SD4 model results and discussion

The calibration of the SD4 model started considering the LU4 calibrated parameters set, which was manually distributed in the three subcatchment considered, taking into account their characteristics. The sensitivity analysis pointed out that the total flow was strongly influenced by H_u, especially for the sericitic schist HRU (likely because a lower PET associated to this north orientated unit amplified the influence of H_u). Observed daily stream flows and the corresponding simulated ones obtained with the SD4 model structure are shown in Fig. 4c. The index E was equal to 0.77, global BE was less than 2% and the greatest simulated peak flow (8.6 m^3/s) was closer to the observed one (Table 2). In general, it can be said that the results obtained from this analysis agree with the one obtained previously for the LU4 model. The major improvement of the SD4 model was a better simulation of the base flow discharges, which was of particular importance in the first year (see Fig. 4c and partial BE for baseflow discharges in Table 2). However, the model could not reproduce the drying-up and wetting-up dynamics (see Fig. 4c and partial BE for extremely dry flows in Table 2) and the number of days with a simulated discharge less than 0.001 m^3/s was only 92 against the 220 observed.

Each one of the new features included into the SD4 model was analysed separately, to understand how they were influencing the model output and why it failed to represent the transition period. Compared to the LU4 model, the introduction of a different set of parameters for each lithological unit in the SD4 model improved the intermediate and base flow simulation: the partial BE decreased from 12.6% to 0.4%, and from 7% to -1% for the intermediate and base flow range, respectively. It also helped to simulate slightly better the peak flows, and therefore E rised up to 0.79 against the 0.72 of the LU4 model. The number of days with a simulated discharge less than 0.001 m^3/s was 224, much better than the 248 obtained with the LU4 model.

The second feature analyzed was the introduction of the two indexes λ(m) and β(m). The index E obtained in this way was almost similar to the one obtained with the LU4 model, the global BE (50%) was much greater than the one calculated with the LU4 model, and the partial BE pointed out that this model structure overestimated the lowest discharge, the base flow and the intermediate flow ranges. The significant increase of total and partial BE was mainly due to a 10% decrease in evapotranspiration, from 600 mm/year (calculated with the LU4 model) to 536 mm/year. The introduction of λ(m) and β(m) only improved the maximum simulated peak flow (up to 8.9 m^3/s), reducing the partial BE associated with the highest flow range. Despite underestimating actual evapotranspiration, λ(m) and β(m) improved the model's ability to reproduce discharge dynamics during the driest year (the first one). This result highlights the importance of characterizing as better as possible the spatial variability of evapotranspiration when modelling catchments such as the Mediterranean ones where vegetation activity is the major driver of the hydrological cycle.

Finally, the inclusion of small reservoirs only affected the extremely dry discharge range. The drying-up period simulation got worse due to the seepage effect, which lasts until the reservoirs get dry. Consequently, the number of days with a simulated discharge less than 0.001 m^3/s decreased to 131 against the observed 220. However, field observations indicate that water from the main reservoir cannot reach the Fuirosos gauge station anymore starting at the beginning of summer, and that the stream begins to dry out from downstream to upstream.

To this end, recent fieldworks at Fuirosos pointed out that there might be, in deed, a loss of water which could be attributed to reverse fluxes from the stream to the near-stream groundwater zone (Butturini et al., 2002) and/or to a high evapotranspiration demand by riparian vegetation, in particular during late spring and summer (Bernal, 2006). Following these evidences and in order to improve the drying-up and wetting-up periods, the next step in the conceptualization process was the introduction of a new tank into the model representing the riparian zone.

6. Fourth Conceptualization: 4-response semi-distributed model plus riparian tank (SD4-R)

6.1 SD4-R model description

The semidistributed model SD4 was finally provided with one more tank representing the riparian zone. The aim was to simulate bi-directional water flux (F_{sr}) between the stream channel and the riparian zone (Fig. 3c). Exchanges of water are generated according to the difference between the river stage d (m) and the riparian water table e (m), following equation 6. When d is higher than e, water will flow from the stream to the riparian zone until the recover of the local riparian water table or the saturation of the maximum capacity of the riparian storage ($H_{r,\ max}$). In this case, F_{sr} will be negative and it has been called “inverse flow”. On the contrary, when e is higher than d, water will flow from the riparian zone to the stream and F_{sr} will be positive, representing the “direct flow”.

$$F_{sr} = K_{sr} \cdot \left(\frac{e-d}{m} \right) \cdot (2 \cdot f \cdot c) \qquad (9)$$

where: K_{sr} is the saturated conductivity between the riparian zone and the stream channel (13 m/day, Butturini et al., 2003); m is one side riparian

zone width (15 m); f is the estimated length of the riparian zone (2,000 m) and c is the estimated elevation of the stream bed over the bedrock (3 m).
The riparian water head (*e*) depends on the actual water content into the riparian tank (after overland runoff and evapotranspiration from the riparian zone are computed) in this way:

$$e = \frac{V_r}{2(m \cdot f) \cdot \phi} \tag{10}$$

where: V_r is the actual content of groundwater in the riparian storage (m^3) and ϕ is the effective porosity of the riparian soil profile (0.45).
The stream water level (d) is a function of the amount of water in the river channel tank and its estimated representative section:

$$d = c + \frac{V_s}{b \cdot f} \tag{11}$$

where: V_s is the actual content of water in the channel tank (m^3) and b is the stream width (5 m).
The water fills the riparian tank also according to an infiltration capacity parameter (K_r) to be calibrated. Water is depleted by evapotranspiration (following equation 2) and overland runoff is produced when infiltration capacity or the riparian maximum capacity are exceeded. For the riparian zone, the potential evapotranspiration correction factor has been set to 1.

6.2 SD4-R model results and discussion

The graphical fit of the transition period improved significantly with the introduction of the riparian tank, as shown in Fig. 4 d. The number of days with a simulated discharge lower than 0.001 m^3/s increased from 92 (model SD4) to 212, that represents a value fairly close to the observed 220.

Interestingly, the riparian tank gave rise to steeper hydrograph recessions during the drying-up period as suggested by McMahon (2005).
In addition, the stream response was delayed in the wetting-up period, since the tank needs to be refilled by inverse flow before generating direct flow. Because of that, simulated stream responses to precipitation episodes, occurring just after the drought period, fall far below the general trend obtained for the remaining part of the year. The SD4-R model resembles quite satisfactorily the non-linear runoff-rainfall relationship shown in Fig. 5 and described by Butturini et al. (2002), reproducing the correspondent inverse flow observed by Butturini et al. (2003) due to the first autumnal storms.

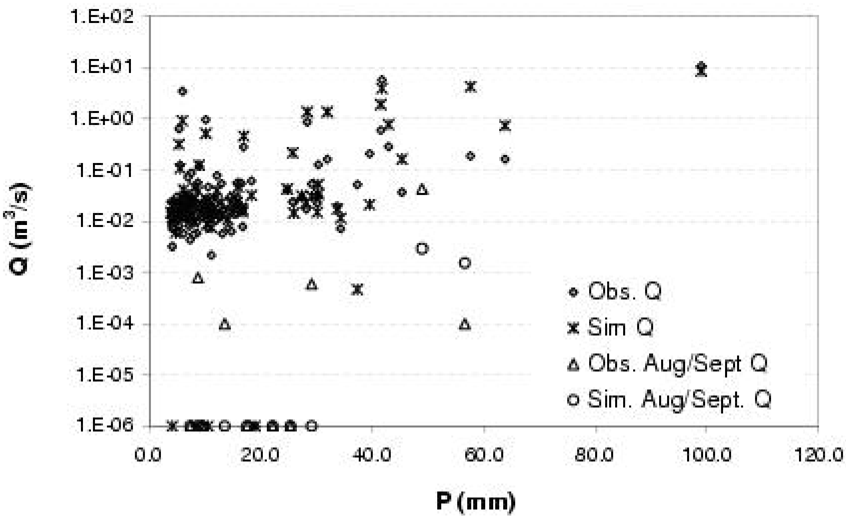


Fig. 5. Relationship between precipitation inputs against observed and simulated discharge (for precipitation episodes ≥ 4 mm) obtained with the SD4-R model.

Our results showed that the riparian tank exerted an important control on low streamflow, despite the fact that evapotranspiration by riparian vegetation represented a small fraction of water loss in annual terms (only 0.7%). The sensitivity analysis of the riparian submodel parameters (H_{rmax} and K_r) revealed that they exerted a very limited influence on the total flow (for a reduction by 50% the effect on total flow was less than 1%)

Moreover, the temporal dynamics of the water level observed in a well located in the riparian area was compared with the temporal dynamics of *e* (Fig. 6). Taking into account *e* is a general level for the entire riparian zone, this represents an additional validation of the model behaviour, since the information about this well and its water table dynamics was not included in the calibration process.

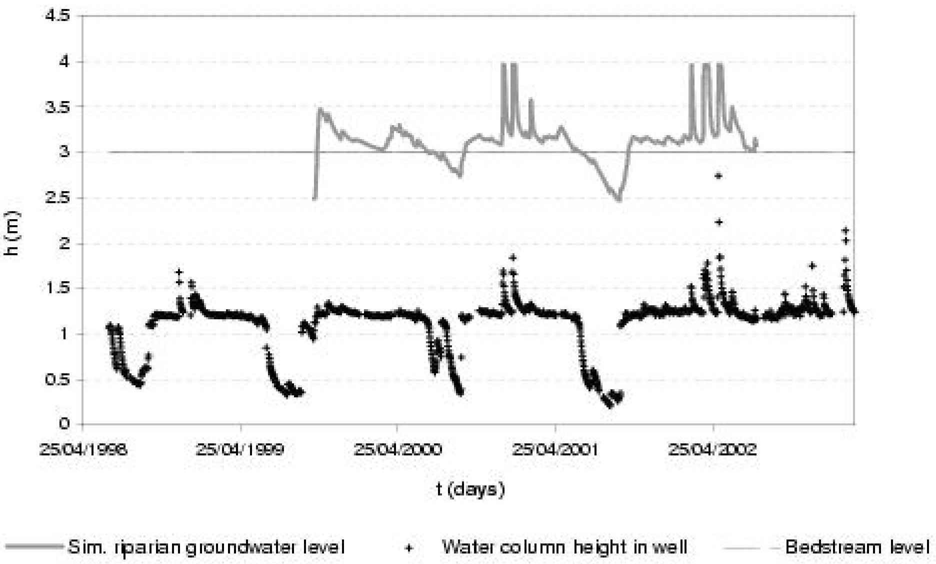


Fig. 6. Comparison of the temporal dynamics between the point water column observed in a well located in the riparian zone near the Fuirosos stream channel and the riparian groundwater table, simulated by the model SD4-R.

7. Validation results

The validation process is an important test to demonstrate the model robustness, since it gives an idea about how the model will perform when it is used in different conditions from those concerning in the calibration process (Andersen et al., 2001). Distributed and semidistributed models allow both temporal and spatial validation. In particular, Vieux (2004) stressed the importance of addressing the later: the model efficiency at interior points of a catchment.

7.1 Temporal Validation

The four model structures were validated against observed data recorded at Fuirosos from the 1st of August 2002 to the 30th June 2003. The statistics are given in Table 3. It is worth pointing out that total precipitation in February 2003 (186.6 mm) was exceptionally high compared with average total precipitation recorded during previous Februaries (37 mm). Moreover, starting in January 2002 precipitation records were from different meteorological stations near the Fuirosos catchment. Such input uncertainty and spatial variability of the precipitation, may reduce the actual model performance, in particular for the highest rainfall events. Consequently, E and BE were calculated with and without including the discharge generated by the most important rainfall episodes of February 2003 (20/02/2003 and 25/02/2003).

The temporal validation of the LU3 model presented, in both cases, very low E and BE higher than 100%. The index E computed considering the most important rainfall events of February 2003 was -0.6 while without considering them it increased to 0.2, which in any case did not represent a satisfactory result. Considering the different discharge ranges it is clear that the LU3 model gave the worst performance, since it overestimated not only the base flow range, but also the intermediate discharges, which related BE was greater than 80%. Moreover, it was not able to represent correctly the drying-up of June 2003 (Q < 0.005 m^3/s). For this reason, it can be said that the LU3 model failed in representing the global catchment hydrological behaviour, also during the temporal validation period.

The temporal validation of the LU4 model presented better E. This index was still low (0.3) when the largest precipitation events of February 2003 were included but it increased to 0.8 when they were excluded. The BE obtained with the LU4 model in the first case was about 25% and in the second case was about 10% (Table 3). In general, the LU4 model improved the representation of all the discharge ranges considered, in particular of the base flow and the intermediate discharge ranges. However, the LU4 model was still not able to represent correctly the drying-up of June 2003 since the stream got dry too early. The associated partial BE was only -0.1% but in absolute terms would be -100%. This suggested that the transpiration, which was a key process during the drying-up, may be overestimated in the LU4 model. In general, it can be said that the LU4 model performed much better than the LU3 model also during the temporal validation period.

Table 3. Temporal validation efficiency indexes: the Nash index (E); the global and the partial balance volume errors (BE); the simulated maximum peak of discharge (Sim. Q)[a]. The period of calibration was from 01/08/2002 to 30/06/2003 (February 2003 included)

Model structure	E	Sim. Q m^3/s	Global BE %	Partial BE % Q < 0.005 m^3/s	Partial BE % 0.005 ≤Q< 0.05 m^3/s	Partial BE % 0.05 ≤Q< 1 m^3/s	Partial BE % Q ≥ 1 m^3/s
LU3	-0.6	3.9	130.0	0.5	35.3	86.9	7.5
LU4	0.3	3.5	25.1	-0.1	3.5	19.0	2.7
SD4	0.3	3.3	27.7	0.9	9.2	16.5	1.1
SD4-R	0.4	3.3	23.6	0.4	6.9	15.3	1.1

[a] The observed maximum peak is 2.7 m^3/s.

The temporal validation of the SD4 model also improved considerably when the precipitation episodes of February 2003 were not considered. In fact, E increased from 0.3 to 0.7 and global BE decreased from 27.7% to approximately 6%. The SD4 model slightly overestimated the base flow range of discharge, while it improved the BE concerning the intermediate discharge range. As in the case of the calibration process, the SD4 model failed to reproduce the drying-up period as indicated by the high relative BE.

The temporal validation of the SD4-R model (Fig. 7) presented an E equal to 0.4 considering the peak flows of February, while in the opposite case E increased to 0.8. The main goal of the SD4-R model, in this case, was to give the best representation of the drying-up period due to the inclusion of the riparian tank, which would have even more importance if the transpiration process from the aquifers would have any limitation. It has also to be pointed out that the SD4-R model slightly improved both the BE concerning the base flow ranges and the BE related with the intermediate flows.

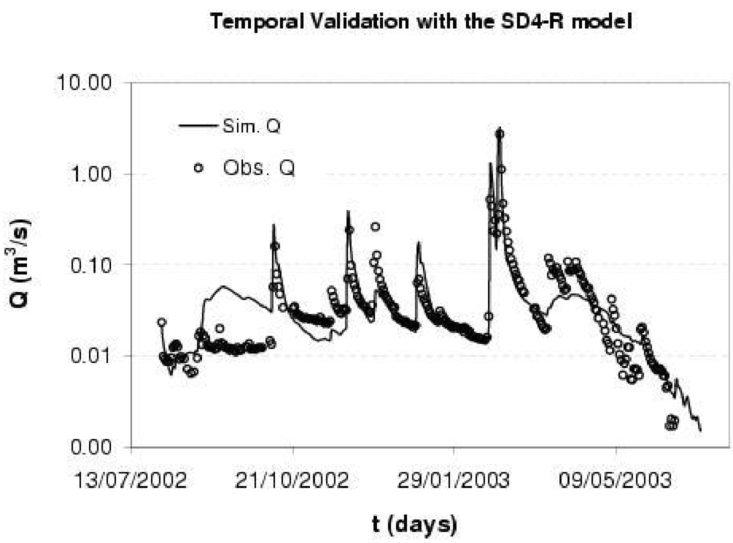


Fig. 7. Observed and simulated daily discharge (m3/s) using the SD4-R model for the temporal validation period (01/08/2002 to 30/06/2003) at Fuirosos catchment.

7.2 Spatial Validation

The spatial validation was carried out considering the measured discharge at the Grimola stream from 18th of September 2000 to 22nd of August 2002 (Table 4). SD4-R was not used because there is not any significant riparian zone in this stream.

The LU3 model overestimated significantly the stream discharge (the BE is higher than 50%) while the E was about 0.6. The number of days with a simulated discharge less than 0.001 m^3/s was 57 against the 82 days (which represents only the 69% of the observed number), mostly between June and August of 2001. Even in this case the analysis considering the different discharge ranges pointed out that the LU3 model gave the worst performance since it generally overestimated both the base flow (in this case, the base flow range is represented also by the discharge less than 0.005 m^3/s) and the higher flow.

Table 4. Spatial validation efficiency indexes: the Nash index (E), the global and the partial balance volume errors (BE); the simulated maximum peak of discharge (Sim. Q)[a]; the simulated number of days with Q < 0.001 m^3/s (Sim. N.)[b]. The period of validation was from 18/09/2000 to 22/08/2002.

Model structure	E	Sim. Q m^3/s	Global BE %	Partial BE % $Q < 0.005$ m^3/s	Partial BE % $0.005 \leq Q < 0.05$ m^3/s	Partial BE % $0.05 \leq Q < 1$ m^3/s	Partial BE % $Q \geq 1$ m^3/s	Sim. N. m^3/s
LU3	0.6	1.8	54.9	15.5	24.4	30.7	-15.7	57
LU4	0.6	1.7	-5.01	4.7	-0.9	9.3	-18.1	97
SD4	0.7	2.5	-4.17	1.8	-10.4	15.5	-11.1	75

[a] The observed maximum peak is 2.7 m^3/s.
[b] The observed number of days with Q < 0.001 m^3/s is 82 days.

Also in the case of the spatial validation, the LU4 model gave better results than the LU3 model. The E was still almost the same (0.6), but the global BE was -5% and the associated partial BE pointed out a significant improvement of the base flow representation. In addition, the number of days with a discharge less than 0.001 m^3/s was 97 against the 82 observed, which was a quite good approximation of the observed dry period at Grimola.

The SD4 model was spatially tested considering that the Grimola subcatchment has two HRUs: one overlying leucogranite and the other sericitic schist. The obtained E was approximately 0.7 and the global BE was -4.17% (Table 4 and Fig. 8). The SD4 model underestimated base flow discharge, suggesting that the percolation to the deep aquifer was overestimated at least at one of the two involved HRU. The number of days with a discharge less than 0.001 m^3/s was 75 against the observed 82 that represents a very good representation of the dry period. This result was coherent with our catchment perception: at Grimola (where there is not a well-developed riparian area exerting a great control on low flow), there is no need to include a riparian tank in the model in order to successfully represent the stream dry period.

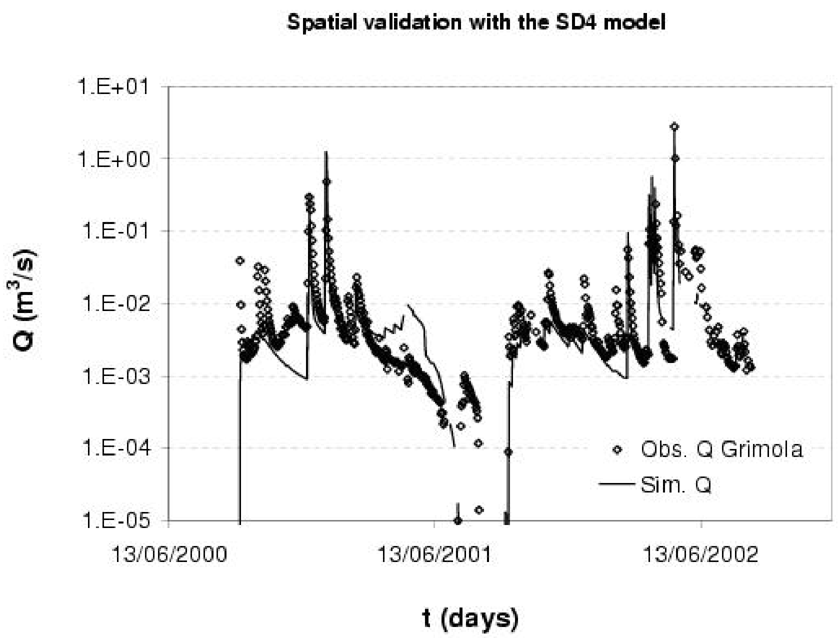


Fig. 8. Observed and simulated daily discharge (m3/s) using the SD4 model for the spatial validation process (from September 18/09/2000 to 22/08/2002) at the Grimola subcatchment.

8. Concluding remarks

Our results suggested that water flowpaths in Fuirosos were essentially different during wet and dry conditions and that several mechanisms can be considered responsible for such non-linear hydrological behaviour. As observed in other Mediterranean catchments (Gallart et al., 2002), our simulations suggested that the permanently saturated zone (deep aquifer) was disconnected from the stream network during the summer dry season and did not contributed significantly to river discharge. At those moments of the year, water from the permanently saturated zone was lost by transpiration rather than by base flow generation, according to our perception. The SD4-R model suggested that the amount of water moved from the saturated zone by plants and capillary forces could be a significant component of the water balance (approximately 21% of the annual actual evapotranspiration). This mechanism could insure plants tolerance to the summer drought, as suggested by Canadell et al. (1996).

According to the SD4-R model, riparian vegetation in Fuirosos contributed to annual evapotranspiration in a small fraction (only 0.7%). Nevertheless, our research points towards the riparian zone as a key compartment for modelling successfully the drying-up period and the non-linear hydrological behaviour of semiarid systems during the wetting-up period. The validation performed in the Grimola stream (that drained a catchment without a well-developed riparian zone) reinforced this result. In addition to that, the present study suggests that the formation of a perched water table is the key hydrological process during the wetting-up period, as observed in other semiarid catchments (Ocampo, 2006). Results presented here suggest that this shallow aquifer may be the main contributor to the discharge during the first two or three months after the summer drought. Only when the catchment saturation becomes high enough during the wet season, the deep percolation recharges the permanently saturated zone and it starts to contribute to the river discharge with a slow base flow.

In semiarid systems, vegetation is the major driver of the annual water balance (e.g., Piñol et al., 1997) and concordantly, our progressive perceptual understanding approach pointed towards the same direction. The 4-response semidistributed model (SD4) highlighted the importance of the spatial variability of the evapotranspiration process in semiarid systems. Furthermore, the model was able to improve the representation of the discharge dynamics during the driest year only when the slope aspect and the vegetation coverage were included into the actual evapotranspiration computation.

The progressive perceptual approach adopted in this study led from an initial lumped structure (LU3 and LU4) to a final semidistributed one that included a riparian tank (SD4-R). This process involved increasing the number of parameters in the model from 6 to 32, and bring about a general improvement of the efficiency indexes (Tables 2 to 4). For the E index in particular, all models were more efficient than LU3, with a p-value < 0.05 (McCuen et al., 2006) and the most complex structures (SD4 and SD4-R) were more efficient than the lumped structures (p-value < 0.05). Both, the calibration and the validation process suggested that the SD4-R model could be the most appropriate structure representing the non-linear behaviour of stream hydrology in semiarid regions (Fig. 9). The results of the temporal and spatial validation results show that the possible overparameterization of this model can be accepted.

The hydrological modelling of semiarid regions such as the Mediterranean ones is a complex challenge and an unresolved problem that could be better addressed by an appropriate conceptualization of these systems. However, this task could only be achieved after the identification of the key hydrological processes governing runoff generation in such systems. Our intention in the present study was an attempt to identify these key hydrological processes and quantify their relative importance by means of progressive perceptual modelling approach (following Piñol et al., 1997). Although it is well-recognized (Blöschl et al., 1995) that, in general, investigative models are more complex in structure and their predictions may be less robust, they allow better insight into a system behaviour. In this way, the influence of the different processes explored in the present study certainly could be extrapolated to improve the representation of other cases (if not the models themselves).

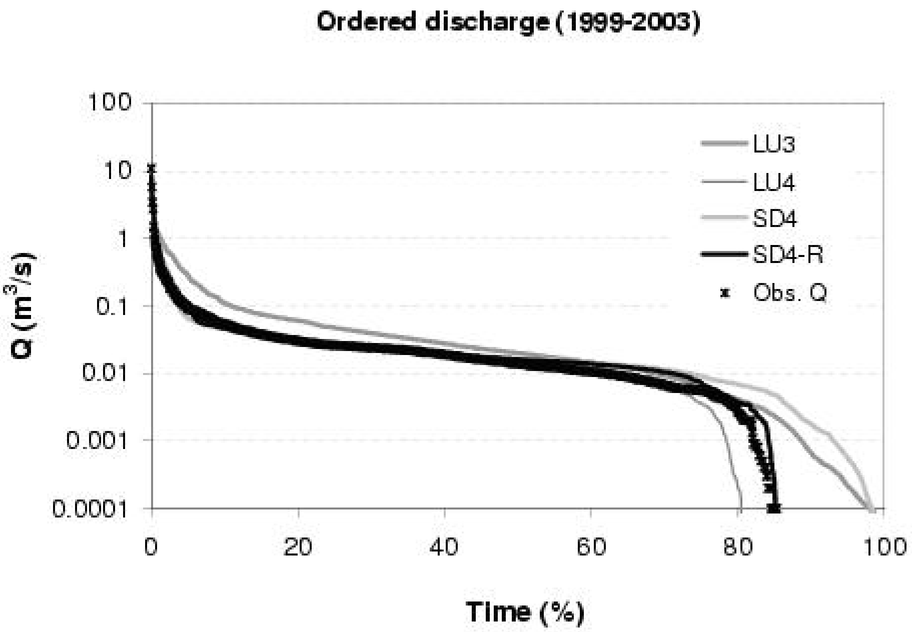


Fig. 9. Observed and simulated ordered daily discharge (m^3/s) from 1999 to 2003 with all the model structures considered in this study (LU3, LU4, SD4 and SD4-R). Note the riparian zone control on low flow.

Acknowledgements

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4.2

Modelling the inorganic nitrogen behaviour in a small Mediterranean forested catchment, Fuirosos (Catalonia)*

Key words

Inorganic Nitrogen; Pulse Behaviour; Riparian Zone

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1. Introduction

Nitrogen is present in both terrestrial and aquatic ecosystems and research is needed to understand its storage, transportation and transformations in river catchments world-wide because of its importance in controlling plant growth and freshwater trophic status (Arheimer et al., 1996; Green et al., 2004; Ocampo et al. 2006; Schlesinger et al 2006; Chu et al. 2008; Vitousek et al. 2009).

Numerous mathematical models have been developed to describe the nitrogen dynamics in cool temperate river-systems, but further work is needed to understand and model the main processes controlling the nitrogen cycle in Mediterranean and semi-arid ecosystems since these systems are not well understood (Avila et al., 1995; Bernal et al., 2005; Wade et al., 2005; Gelfand et al, 2008).

Mediterranean catchments are characterized by a complex hydrological behaviour that causes high inter and intra-annual variability in flow (Gallart et al., 2002). Consequently, models developed for temperate climates generally fail when applied to Mediterranean catchments (Bernal et al., 2004). Mediterranean ecosystems are subjected to severe drought periods followed by intense rainfall events, which produce alternate dry and humid conditions that influence the soil microbial activity (Austin et al., 2004, Reynolds et al., 2004, Schwnning et al., 2004b). Models based on a representation of temperate climates do not represent this rapid transition from dry to wet periods well. Birch (1959, 1960, and 1964) was one of the first to characterize the impacts of soil drying and wetting cycles on mineralization and nitrification, demonstrating that rapid mineralization follows rewetting of dry soil and that in continuously moist conditions there is a release of nitrogen, much of it as nitrate. Many other authors stressed the influence that wet-dry cycles have on microbial biomass (Van Gestel et al., 1993), denitrification (Mummey et al., 1994, Peterjohn and Schlesinger 1991) and ammonia volatilization (Heckathorn and Delucia, 1995).

Schiwinning et al. (2004a, 2004b) spoke about a “pulse dynamic” in arid and semi-arid ecosystems, considering the rainfall inputs to a dry soil as triggers of a cascade of biogeochemical and biological transformations. According to Schiwinning et al. (2004a, b), precipitation applied to a dry soil surface creates a pulse of soil moisture that can be characterized by the depth to which soil water potentials are elevated to levels that promote biological activity and the length of time over which water potentials remain at biologically relevant levels.

Intermittent streams and their associated riparian zone have been highlighted as ‘hot spots’ for biogeochemical processes in arid and semi-arid regions (McIntyre et al., 2009). Bernal et al. (2007) suggested that Mediterranean riparian soils act as source or sink of dissolved nitrogen depending on the period of the year, mainly due to contrasting soil moisture condition between the dry and the wet period. Moreover, Butturini et al. (2003) suggested the unsaturated riparian soil of the Fuirosos catchment, a small intermittent Mediterranean stream in Catalonia (Spain), as a possible source of nitrate, especially after the summer drought, which can be rapidly mobilized due to the formation of a rising riparian groundwater table into the unsaturated upper soil layer adjacent to the stream channel.

The nitrogen dynamics of the Fuirosos catchment were analysed previously with the process-based Integrated Catchment Model of Nitrogen (INCA-N) model (Whitehead et al., 1998; Wade et al., 2002, Bernal et al., 2004). INCA-N was developed for temperate regions and has been demonstrated to simulate properly the hydrology and nitrogen dynamics observed in these types of ecosystems (Wade et al., 2004). The model gave unsatisfactory result for the Fuirosos catchment suggesting that key processes were missing (Bernal et al., 2004).

The present research aims to develop a new model to represent the inorganic nitrogen response in Mediterranean catchments using INCA-N as a basis for the equations implemented, but including additional mechanisms to take into account the ideas and results pointed out before and obtained in previous studies in semi-arid and Mediterranean catchments. Namely, these new elements are: biological thresholds responses to soil moisture in order to reproduce the pulse dynamic observed in such environment; a specific function for the soil moisture correction factor for the mineralization process; nitrification and denitrification processes associated to the shallow perched water table and finally, the introduction of a riparian zone compartment. The nitrogen model scheme developed in this study was coupled to already existent hydrological conceptual models previously applied to the Fuirosos catchment (Medici et al., 2008).

2. N-model description

The hydrological behaviour of the Fuirosos catchment has been successfully modelled previously (Medici et al., 2008). A key result of this previous study is that the perceptual model including four different catchment hydrological responses (direct flow, interflow, quick and slow base flow) is the most suitable to simulate the discharge at Fuirosos.

The initial lumped conceptual model proposed (LU4) was developed into a semi-distributed form (SD4-R) in which the spatial variability of the evapotranspiration according to the vegetation cover and the local aspect was considered. In the final semi-distributed structure of the hydrological model (which gave a best fit of 0.78 in term of Nash & Sutcliffe index) an additional conceptual store representing the riparian zone was included, as well as the four reservoirs present in the catchment.

In the current work, the previous cited models were extended to include processes representing the inorganic nitrogen cycle to simulate the nitrate and ammonium concentration observed in the Fuirosos stream. Therefore, the progressive perceptual approach adopted led from an initial lumped structure (LU4-N) to a very simple semi-distributed one (LU4-R-N) that included the riparian tank along with the four small reservoirs and eventually to a more complex semi-distributed one (SD4-R-N) that included the riparian zone, the four reservoirs as well as catchment spatial variability to some extent.

The first approach to simulate the transport, storage and transformations of nitrogen in the terrestrial and aquatic components of the catchment was done using the lumped hydrological (LU4) model as a basis. The LU4-N model integrates hydrology, soil and shallow aquifer N processes, and simulates daily NO_3-N and NH_4-N concentrations in the stream. The soil nitrogen cycle conceptual model includes the mineralization process and non-biological nitrate fixation modelled using zero order kinetics. The processes of nitrification, ammonium bacterial immobilisation, ammonium and nitrate soil plant uptake, abiotic absorption and denitrification are included and represented using first order kinetics.

The total number of parameter to be calibrated for the LU4-N model is 28 of which 9 are for the rainfall-runoff sub-model and 19 for the N sub-model. A perceptual model which shows the key nitrogen stores and pathways is presented in Figure 2. At present, the only source of N is atmospheric deposition as this is the main input of nitrogen in the catchment but other anthropogenic sources could be included in future versions if required. For the deposition, the estimated values obtained by Rodá et al. (2002), after Bernal et al. (2004) were used. Namely: the wet deposition of inorganic N was 5.7 kg N ha^{-1} yr^{-1} (52% as ammonium and 48% as nitrate), while the dry deposition of inorganic N was 9.2 kg N ha^{-1} yr^{-1} (45% as ammonium and 55% as nitrate). The model equations were written in terms of N mass and water volume and a daily time step was adopted. The equations were solved sequentially (i.e. for the soil ammonium cycle: first of all mineralization, secondly immobilization then plant uptake and finally nitrification) and it was verified, taking into account several different sequences, that the particular one adopted did not significantly affect the model results. In both shallow and deeper aquifer, N uptake associated with the transpiration flux is assumed to occur, which depends on the simulated ammonium and nitrate concentration in each aquifer, on the amount of water transpirated by plants and finally on the annual maximum solute uptake.

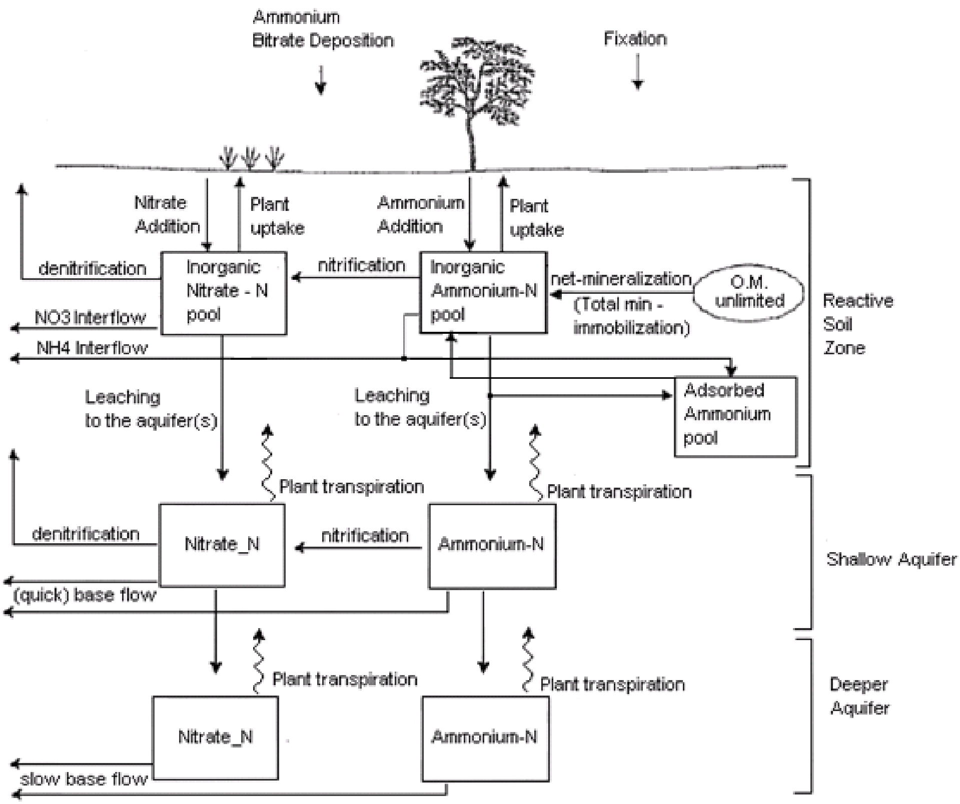


Fig. 2. Nitrogen cycle in the soil and aquifers systems for the LU4-N model (modified from Whitehead et al. 1998).

All the soil processes are adjusted by a soil moisture factor ($S_{1\_Process}$) to represent the moisture control on bacterial processes and are temperature dependent (Whitehead et al., 1998; Wade et al., 2002). Moreover, a different soil moisture threshold (U) has been introduced for each soil process to determine activation. The concept of a threshold response is not new in arid land ecology (Reynolds et al., 2004, Schwnning et al., 2004a). Traditionally this concept has been related with the ecosystem primary production, though Schwnning and Sala (2004) generalized the threshold paradigm to a wide range of ecosystem processes. In fact, they suggested that the hierarchy of pulse events has a corresponding hierarchy of ecological responses that is determined by the ability of organism to utilize soil moisture pulses of different duration, infiltration depths and soil water potential. As a matter of example, the mineralization processes is described as:

$$M_{NH4\_Miner}(t) = K_{Miner} \cdot S_{1\_Miner}(t) \cdot TF \tag{1}$$

where: M_{NH4_Miner} is the ammonium mineralized mass (kg N ha^{-1} day^{-1}) in a time step; K_{miner} is mineralization rate constant (kg N ha^{-1} day^{-1}) and TF is temperature factor, according to Wade et al. (2002) and S_{1_Miner} is the soil moisture factor, which is calculated as follows:

$$\begin{aligned} S_{1\_Miner}(t) &= \frac{H_1(t) - IA}{U_{Miner}} \quad if \quad 0 \le H_1(t) - IA \le U_{Miner}\left(\le H_u^*\right) \\ S_{1\_Miner}(t) &= 1 - \frac{\left(H_1(t) - IA - U_{Miner}\right)}{\left(H_u^* - U_{Miner}\right)} \quad if \quad U_{Miner} < H_1(t) - IA \le H_u^* \end{aligned} \tag{2}$$

where: H_1 is the actual static storage water content (mm) and Hu* is the maximum static storage water content (mm) (where the static tank represents water that can leave the catchment only by evapotranspiration); IA are the initial abstractions (interception and water detention in puddles) which were (approximately) estimated as 19 mm day^{-1}; t is the time step (day) and U_{Miner} is the soil moisture threshold for mineralization (mm), which is expressed as a percentage of H_u^*.

According to equation 2, the S_{1_Miner} factor has a triangular shape with a maximum value when the soil moisture content is equal to U_{Miner}. This is consistent with McIntyre et al. (2009), who found that mineralization is reduced under soil moisture content close to saturation, but increases under moderate soil moisture content. For the other soil nitrogen processes, the corresponding soil moisture factors are computed according the following general expression:

$$
\begin{aligned}
&S_{1\_\mathrm{Pr}ocess}(t)=0 \quad if \quad 0 \leq H_1(t)-IA \leq U_{\mathrm{Pr}ocess}\left(\leq H_u^*\right) \\
&S_{1\_\mathrm{Pr}ocess}(t)=\frac{\left(H_1(t)-IA-U_{\mathrm{Pr}ocess}\right)}{\left(H_u^*-U_{\mathrm{Pr}ocess}\right)} \quad if \quad U_{\mathrm{Pr}ocess}<H_1(t)-IA \leq H_u^*
\end{aligned}
\tag{3}
$$

where: $U_{Process}$ is the generic soil moisture threshold for the soil process included in the model (except mineralisation); $S_{1\_Process}$ is the soil moisture factor for any soil nitrogen process. Thus for any soil N process, except mineralization, a minimum soil moisture content is needed for the process to be activated.

Table 1. Parameters considered in each of the three structures (LU4-N, LU4-R-N and SD4-R-N) and their effective values after calibration process

	Parameters	Description	LU4-N	LU4-R-N		SD4-R-N			
			Basin	Hill-slope	Rip. Z	Leucogr.	Granod.	Schist	Rip. Z
Nitrogen model calibrated parameters									
1	K_{min}	Hillsolpe mineralization rate [Kg N ha^{-1} day^{-1}]	0.51	0.51	3.5	0.5			3.3
2	K_{nitr}	Nitrification rate [day^{-1}]	1.0	0.6	1.0	1.0			2.2
3	K_{denitr}	Denitrification rate [day^{-1}]	0.1	0.08	1.8	0.04			1.17
4	K_{imm}	Immobilization rate [day^{-1}]	0.15	0.1	0.01	0.34			0.53
5	K_{upNO3}	Nitrate plant uptake rate [day^{-1}]	50	2.04	2.04	44.15			63.04
6	K_{upNH4}	Ammonium plant uptake rate [day^{-1}]	50	4.39	4.39	8.28			77.34
7	K_{denitr_aquif}	Shallow aquifer denitrification rate [day^{-1}]	0.06	0.06	0.03	0.22			0.11
8	K_{nitr_aquif}	Shallow aquifer nitrification rate [day^{-1}]	1.84	1.84	1.97	0.97			0.18
9	K_{ads}	Ammonium soil adsorption rate [day^{-1}]	0.88	0.88		0.82			
10	K_{des}	Ammonium soil desorption rate [day^{-1}]	0.05	0.05		0.5			
11	U_{min}	Mineralization soil moisture threshold (% Hu*)	48.2	48.2	36.8	56.0			22.9
12	U_{nitr}	Nitrification soil moisture threshold (% Hu*)	57.2	57.2	34.0	63.0			34.0
13	U_{denitr}	Denitrification soil moisture threshold (% Hu*)	89.7	78.6	67.0	85.0			93.7
14	U_{immob}	Immobilization soil moisture threshold (% Hu*)	41.6	41.6	68.8	92.0			94.0
15	C_9	Maximum temperature difference (ºC)	6.15	6.15		6.15			
16	$MaxAds_{NH4}$	Daily max. NH_4 adsorption [kg N day^{-1} km^{-2}]	14.5	14.5		36.14			
17	$MaxUP_{NH4}$	Annual max. NH_4 uptake [Kg N ha^{-1} day^{-1}]	90.1	90.1		97.9			
18	$MaxUP_{NO3}$ (1)	Annual max. NO_3 uptake [Kg N ha^{-1} day^{-1}] (December, January and February)	21.6	21.6		18.5			
19	$MaxUP_{NO3}$ (2)	Annual max. NO_3 uptake [Kg N ha^{-1} day^{-1}] (Rest of the year)	118.0	118.0		54.44			

The LU4-N model was then evolved to a simple semi-distributed structure splitting the catchment into two Hydrological Representative Units (HRUs): (1) the riparian zone that represents approximately 0.5% of the total catchment area, corresponding to a part of the alluvial zone that goes along the edge of the river; and (2) the rest of the catchment (hill-slope hereafter).

In this way two different parameters sets were considered, one for each HRU. The LU4-R-N considers neither the spatial variability of the evapotranspiration nor that of the lithology. The LU4-R-N model requires 42 parameters to be calibrated, of which 11 for the rainfall-runoff model and 31 for the N sub-model (12 specific for each HRU and 7 common for the whole catchment) (Table 1).

The aim with this model structure was to analyze the possible effect of the riparian zone on nitrate release to the stream. The LU4-R hydrological model and the N sub-model were coupled following the scheme shown in Figure 3. The hydrological conceptual scheme adopted for the semi-distributed model differs slightly from that published in Medici et al. (2008). In this case, part of the hill-slope discharge (corresponding to the area not drained by the four small reservoirs, which represents approximately 37% of the total catchment area) is routed through the riparian storage before reaching the stream channel (Fig. 3). This change does not affect the hydrology simulation considerably, but is thought to be relevant for simulating solute behaviour. We assumed that the main effect of the four reservoirs mainly was dilution on nitrate and ammonium concentration.

In a next phase of development, the LU4-R-N was extended to include the spatial variation in evapotranspiration and lithology (SD4-R-N). As such, the catchment was divided into 4 HRUs: the three main catchment lithological units (leucogranite, granodiorite and sericitic schists, all together cited in this paper as hill-slope zone) and the riparian zone, as those used in the application of the SD4-R hydrological model (Medici et al., 2008). Thus, the PET spatial variability for the actual evapotranspiration computation was included taking into account the representative vegetation cover and the potential sunshine arriving to each lithological unit according to its representative aspect and surrounding relief. The parameterization of the 4-HRUs was done for the rainfall-runoff sub-model only; for the N sub-model, only the riparian and reminder of the catchment HRUs were considered for parameterization (Table 1). In this case, the total number of parameters to be calibrated for the hydrological model is 28, while for the N model is still 31 as for the LU4-R-N model.

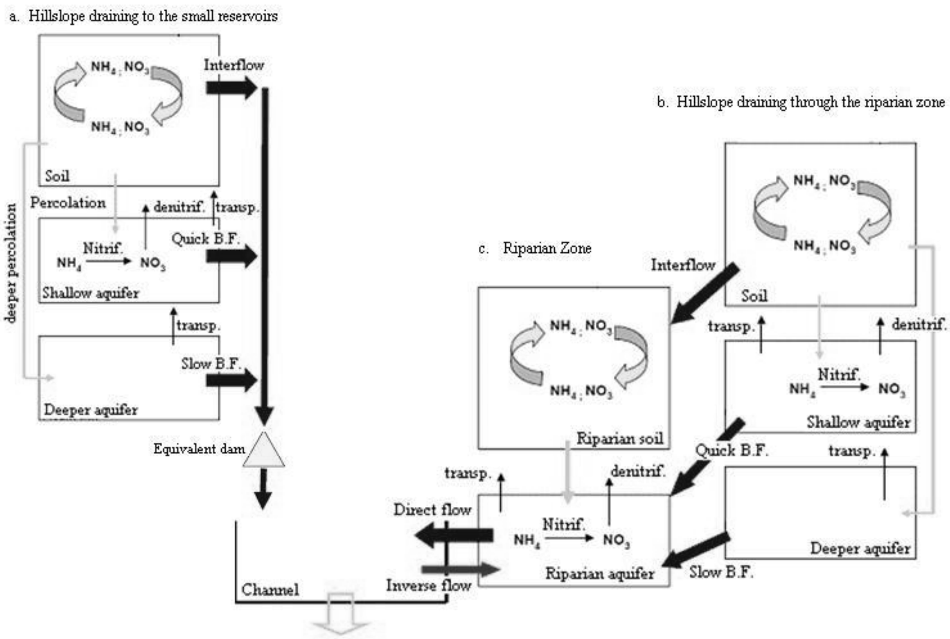


Fig. 3. LU4-R-N and SD4-R-N conceptual scheme, where a) represents the part of the catchment that drains to the four small reservoirs located at the catchment; b) represents the part of the catchment that drains through the riparian zone before reaching the stream channel and finally c) represents the riparian zone which presents a bidirectional flow with the channel.

3. Results

The calibration period covers approximately three hydrological years from October 1999 to August 2002, while the temporal validation one considers the period from August 2002 to June 2003 (that means that the model was tested using a period of observed data different from the one used for the calibration process). Only nitrate concentrations were available for the temporal validation process. Parameters were optimized taking into account the Nash and Sutcliffe efficiency index (E), the balance error in terms of observed and simulated global loads (BE) (where the term “global” refers to the whole calibration or validation period), the graphical fit between observed and simulated N time-series, the relative Root Mean Square Error (RMSE) index and the coefficient of determination (r^2).

The calibration was done by an automatic process, namely Evolver 4.0 for Excel (32-bit) and then by final manual adjustment of the parameters to check the behaviour of the model. For the LU4-N model the same parameters determined in the study by Medici et al. (2008) were adopted for the hydrology simulation, so therefore only the 19 N-model parameters were calibrated in this study (Table 1).

On the other hand, in the case of the semi-distributed models (LU4-R-N and SD4-R-N), the rainfall-runoff model was calibrated first and afterwards the N sub-model. Because of the different hydrological scheme adopted for this study, the parameters set for the hydrology slightly differed to that proposed in Medici et al. (2008) without representing any relevant change worthy of attention. The parameter values determined in the calibration of each of the three nitrogen sub-model structures are shown in Table 1. The goodness-of-fit measures for the calibration and validation periods are summarized in Tables 2 and 3 respectively.

Table 2. Calibration goodness of fit indexes (from 13/10/1999 to 22/08/2002): the global and annual Nash index (E; where E=1 is the optimum); the global balance volume errors (BE); the coefficient of determination (r^2) (only shown when $p<0.01$) and the relative Root mean square error (Relative RMSE; where RMSE=0 is the optimum)

	LU4-N			LU4R-N			SD4R-N		
Index	Q	NO3	NH4	Q	NO3	NH4	Q	NO3	NH4
E_{TOT}	0.71	0.46	< 0	0.70	0.56	< 0	0.78	0.68	<0
$E_{1 yr}$	0.62	< 0	< 0	0.50	0.45	0.2	0.52	0.49	0.35
$E_{2 yr}$	0.62	0.47	< 0	0.61	0.43	< 0	0.43	0.57	<0
$E_{3 yr}$	0.74	0.43	< 0	0.72	0.48	< 0	0.86	0.66	<0
BE_{TOT} %	-1.24	-21.95	-30.2	-3.07	-0.48	-14.9	7.52	-8.22	21.03
r^2	0.77	0.5	n.s.	0.78	0.58	0.02	0.78	0.69	0.05
Relative RMSE	0.53	0.56	1.25	0.55	0.50	0.92	0.47	0.43	0.90

Table 3. Validation goodness of fit indexes (from 01/08/2002 to 30/06/2003): the global and annual Nash index (E; where E=1 is the optimum); the global balance volume errors (BE); the coefficient of determination (r^2) (only shown when $p<0.01$) and the relative Root mean square error (Relative RMSE; where RMSE=0 is the optimum)

	LU4-N		LU4R-N		SD4R-N	
Index	Q	NO3	Q	NO3	Q	NO3
E_{TOT}	0.48	<0	0.61	0.40	0.5	0.32
BE_{TOT} %	28.37	-30.2	24.17	-6.0	47	7.12
r^2	0.78 ($p<0.01$)	0.2 ($p<0.01$)	0.77 ($p<0.01$)	0.4 ($p<0.01$)	0.74 ($p<0.01$)	0.4 ($p<0.01$)
Relative RMSE	0.69	0.96	0.60	0.50	0.68	0.53

3.1 LU4-N calibration and validation results

Observed nitrate and ammonium daily stream concentrations at Fuirosos and the corresponding simulated ones, obtained with the LU4-N model structure, are shown in Fig. 5a. The LU4-N model reproduced quite satisfactorily the observed daily nitrate concentrations for the calibration period (E=0.46). According to this model conceptualization, the main pathway controlling nitrate flushing is the flow derived from the shallow aquifer.

As a matter of example, to reproduce the highest nitrate peak observed during March 2002 (Fig. 5a) the LU4-N model simulated, during the previous months, a huge accumulation of ammonium in soil that due to a significant rainfall event (almost 40 mm/day) percolated to the shallow aquifer where it was rapidly nitrified to nitrate. This nitrate rapidly reached the stream being transported with the water flowing from the shallow aquifer to the stream.

The LU4-N model rarely generates interflow, which in general is associated with rainfall largest events (> 40 mm day^{-1}) during the wet period, so it is the responsible for the nitrate flushing just in very few occasions. For example: the observed nitrate peak of the second year simulated (December 2000) it was a large simulated pulse of nitrification in the soil (almost 130 kg N km^{-2} day^{-1}) that caused a major flush of nitrate transported with interflow. In fact, the model simulated an earlier ammonium increase in soil that was rapidly nitrified when the soil moisture content exceeded the threshold for nitrification as a result of a large rainfall event (43 mm day^{-1}) (Fig. 4).

This nitrification pulse dynamic reproduced in terms of average annual loads a Mineralisation:Nitrification (M:N) ratio of 10:1, which is consistent with the results of Serrasolses et al. (1999).

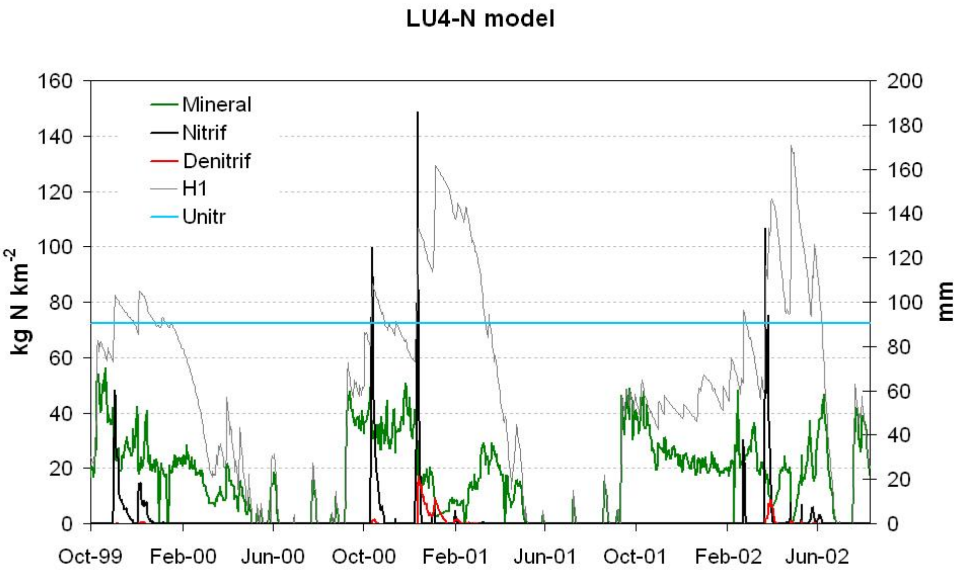


Fig. 4. Simulated soil moisture content (H_1) and nitrification soil moisture threshold (U_{nitr}) in mm, plus mineralization, nitrification and denitrification processes (kg N km^{-2}) for the calibration period (1999-2002) with the LU4-N model

On the other hand, it is worthy to notice that the daily simulated M:N ratio can achieve much higher values or it can also take values between zero and one (that means that nitrification overcomes mineralization), when a huge peak of nitrification takes place (Fig. 6).

Concerning the simulation of streamwater ammonium concentrations, the LU4-N model could not reproduce the observations (E<0) and the statistical relation between the simulated and observed data was not significant (Table 2).

Despite the good results obtained for the calibration of the stream daily nitrate concentrations, the LU4-N model gave poor results for the validation period (Table 3). The model overestimated the nitrate concentration from August to October 2002, due to excessive nitrate amount carried by the base flow and the streamwater nitrate concentrations observed during late autumn and winter 2002-2003 were underestimated (Fig. 7a). A simple one-at-a-time perturbation sensitivity analysis highlighted that the mineralization related parameters (K_{min} and U_{min}), along with the maximum static storage water content (H_u^*) and the maximum annual ammonium plant uptake ($MaxUP_{NH4}$) had the major impact on the nitrate related objective functions. Ammonium soil adsorption rate (K_{ads}) and the nitrification soil moisture threshold (U_{nitr}) were also highlighted as quite sensitive parameters considering the ammonium related objective functions.

3.2 LU4-R-N calibration and validation results

Observed nitrate and ammonium daily stream concentrations at Fuirosos and the corresponding simulated ones, obtained with the LU4-R-N model structure, are shown Fig. 5b.

The obtained discharge efficiency and goodness indexes for the calibration period are similar to those obtained from the simulations done using the LU4-N model (Table 2). This occurs in part because the calibrated parameters for the hydrological components of the models are similar. Though, the nitrate simulation for the calibration period improved. The global E index for the daily nitrate concentration increased to 0.56, and the global BE error decreased to approximately -15%, despite the fact that the LU4-R-N model largely underestimated the highest nitrate concentration peak observed during March 2002 (Fig. 5b).

The LU4-R-N model reproduced the nitrate concentration peak observed during April 2002 that was not simulated by the LU4-N model. During this occasion, because of a large rainfall event (almost 64 mm day^{-1}) the two models could generate nitrate that washed from the soil with interflow at approximately the same rate. However, in the case of the LU4-R-N model, part of the interflow passed through the riparian zone soil (Fig. 3) mobilizing nitrate previously accumulated in this pool. It has to be noticed that in the riparian soil, the simulated mineralization process occurred at a significantly higher rate than in the hill-slope soil and the nitrification process followed more closely the pattern of simulated mineralization being activated more easily than in the hill-slope area (Fig. 8).

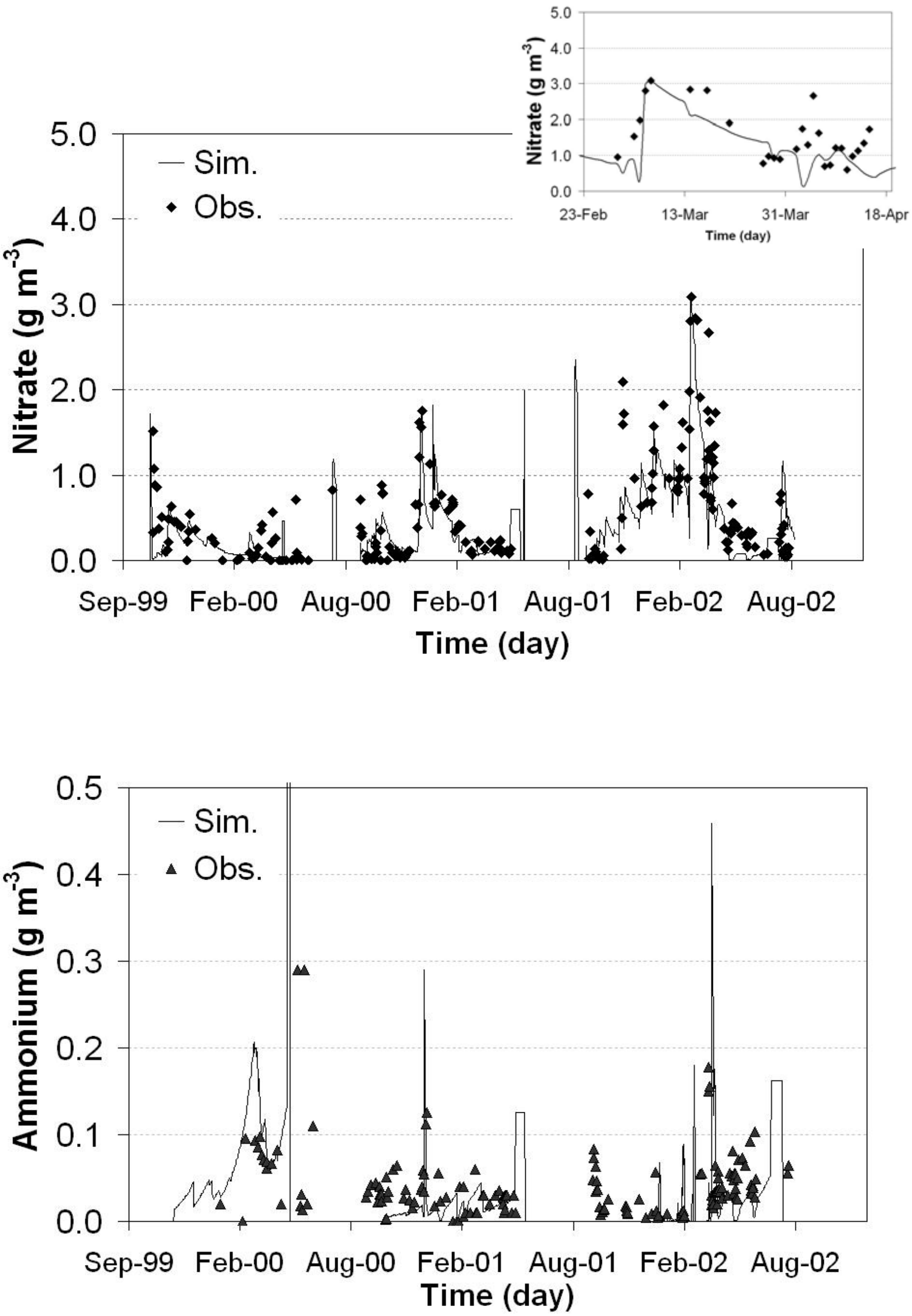


Fig. 5a. Simulated and observed nitrate and ammonium (g N m^{-3}) for the calibration period (1999-2002) with the lumped LU4-N model.

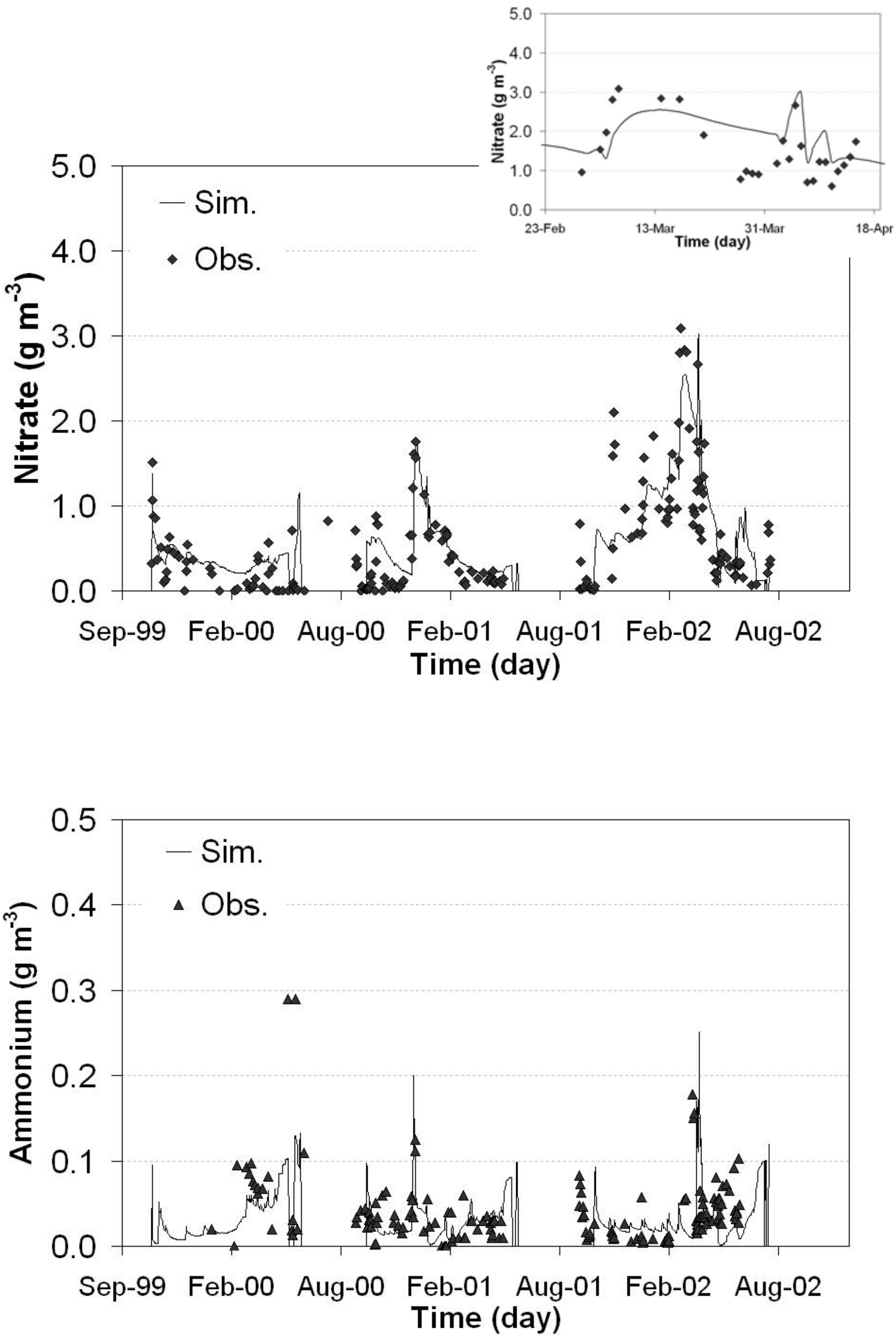
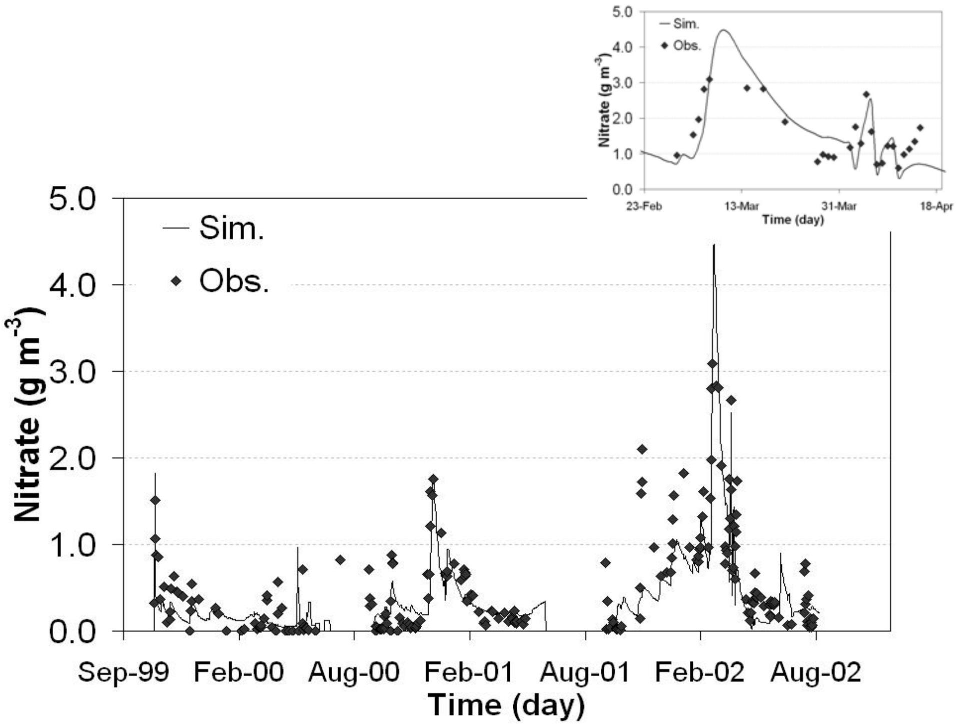


Fig. 5b. Simulated and observed nitrate and ammonium (g N m^{-3}) for the calibration period (1999-2002) with the semidistributed LU4-R-N model (2 HRUs).



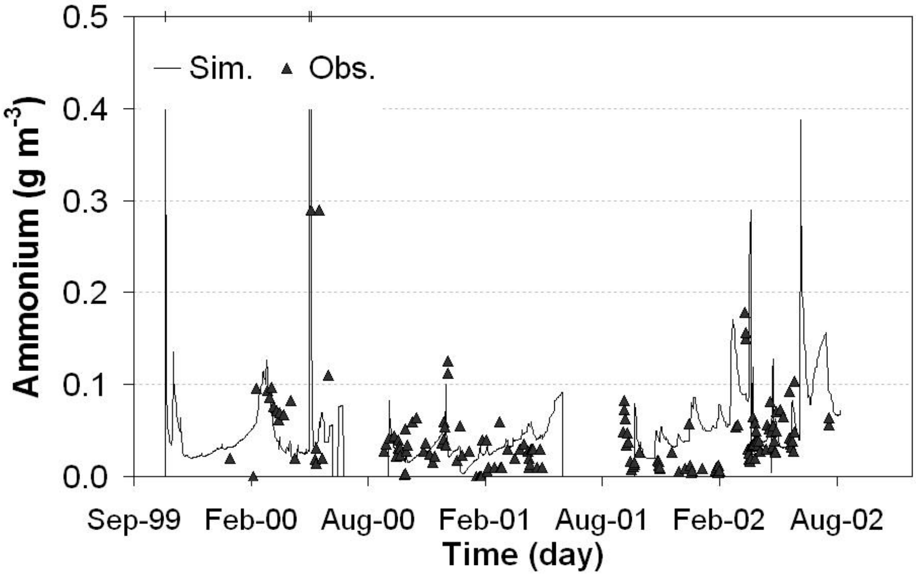


Fig. 5c. Simulated and observed nitrate and ammonium (g N m^{-3}) for the calibration period (1999-2002) with the semidistributed SD4-R-N model (4 HRUs)

Therefore, the simulated annual M:N ratio in the riparian zone was almost 1:1 as well as the daily M:N ratio, while in the hill-slope zone the M:N ratio showed a higher variability as in the case of the lumped LU4-N model (Fig. 6). This dynamic allowed a significant amount of nitrate to be accumulated in the riparian soil, which was available to be rapidly flushed away by interflow derived from the hill-slope soil, as observed in April 2002.

The temporal validation process gave better results for the LU4-R-N model than for the LU4-N model (Table 3 and Fig. 7b). In particular, the introduction of the riparian zone allowed reproducing the nitrate concentration peak observed during March 2002 due to the same mechanism aforementioned (i.e.: previous nitrate accumulation in the riparian upper soil that is afterwards flushed away by interflow derived from the hill-slope soil).

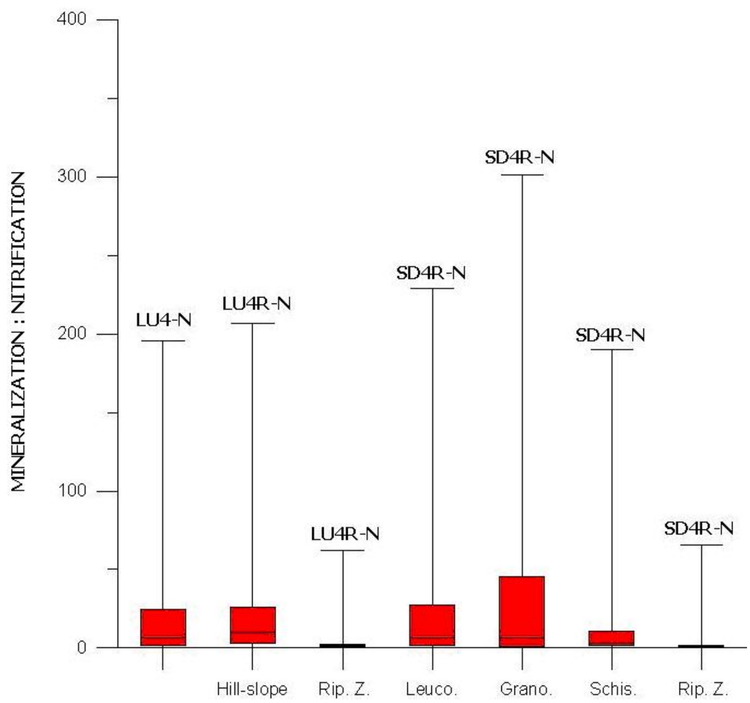


Fig. 6. Simulated Mineralization:Nitrification ratio (M:N) variation according to the different models structures and to each HRU considered.

Finally, the LU4-R-N model failed to reproduce the observed stream daily ammonium concentration. There was only a weak statistical relation between the observed and simulated streamwater ammonium concentrations (r^2=0.02; p<0.1). The positive E index for the first hydrological year (Table 2) represents a slight improvement from the result obtained for ammonium simulations with the LU4-N model.

A simple one-at-a-time perturbation sensitivity analysis highlighted that hillslope and riparian mineralization related parameters (K_{min} and U_{min}), maximum static storage water contents (H_u^*), riparian denitrification related parameters (K_{denitr} and U_{denitr}) and the maximum annual ammonium plant uptake ($MaxUP_{NH4}$) had the major impact on the nitrate related objective functions. Ammonium soil adsorption rate (K_{ads}) and the hillslope nitrification soil moisture threshold (U_{nitr}) were also highlighted as quite sensitive parameters considering the ammonium related objective functions.

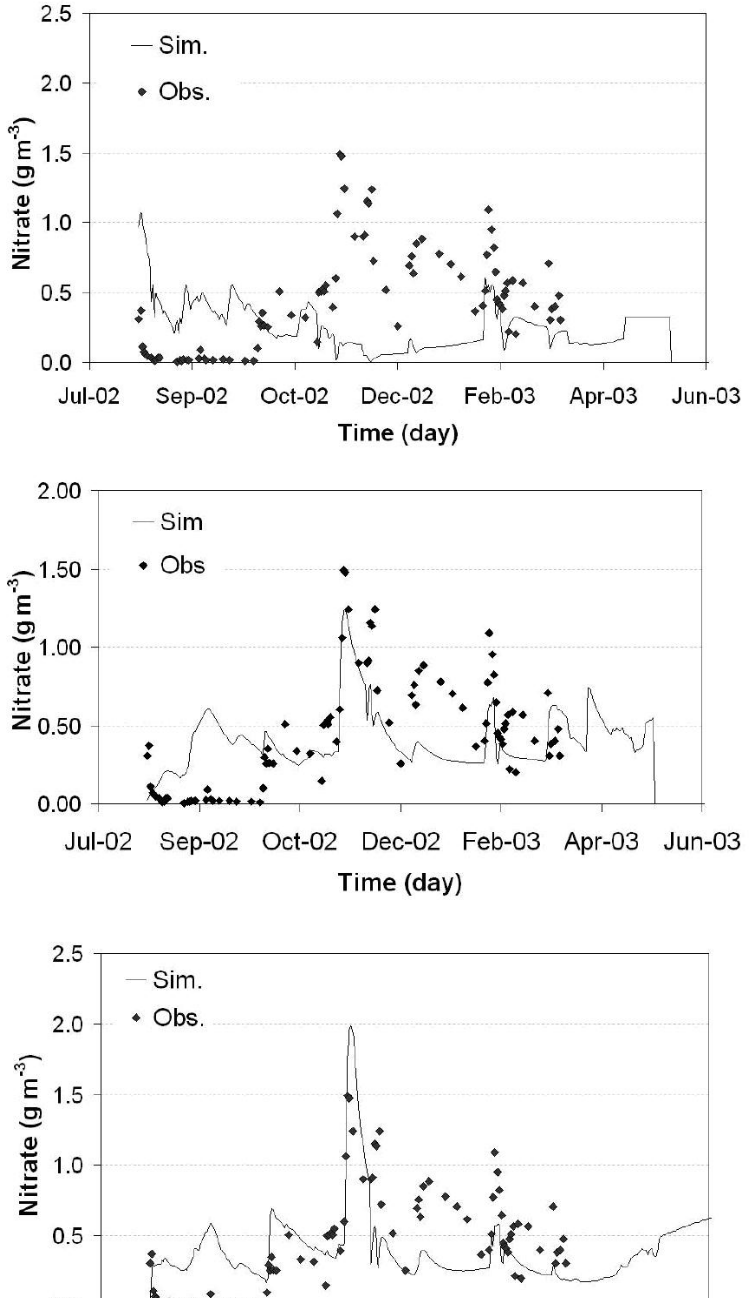
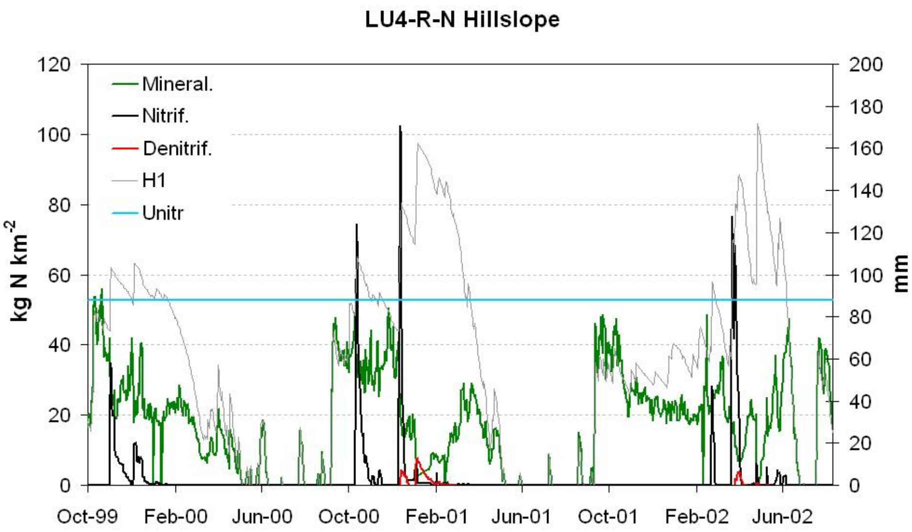


Fig. 7. Simulated and observed stream nitrate concentration (g N m^{-3}) for the validation period (1999-2002) with a) LU4-N; b) LU4-R-N (with 2 HRUs) and c) SD4-R-N (with 4 HRUs).

a.



b.

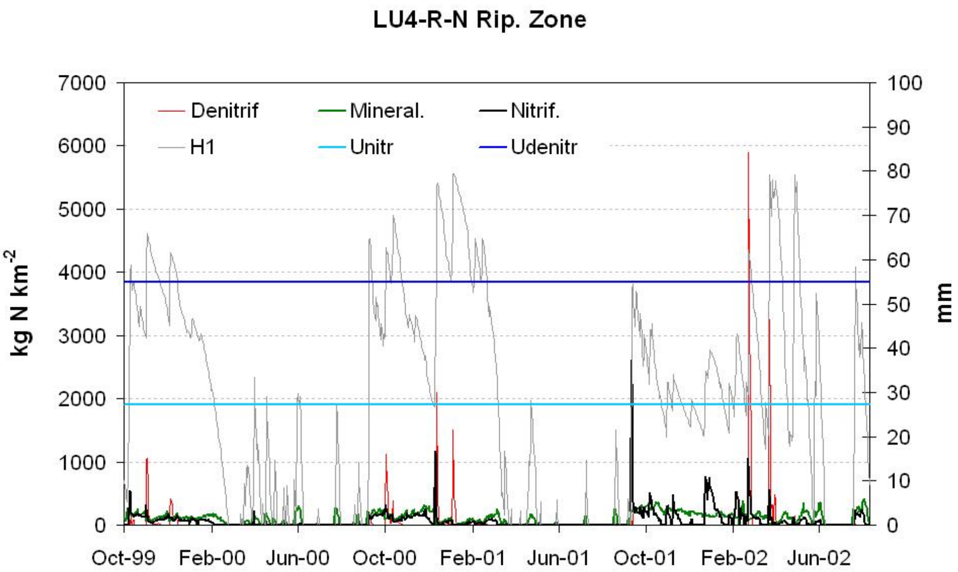


Fig. 8. Simulated soil moisture content (H_1), nitrification soil moisture threshold (U_{nitr}) and denitrification soil moisture threshold (U_{denitr}) in mm, plus simulated mineralization, nitrification and denitrification processes (kg N km^{-2}) for the riparian zone (calibration period 1999-2002) with the LU4-R-N model

3.3 SD4-R-N calibration and validation results

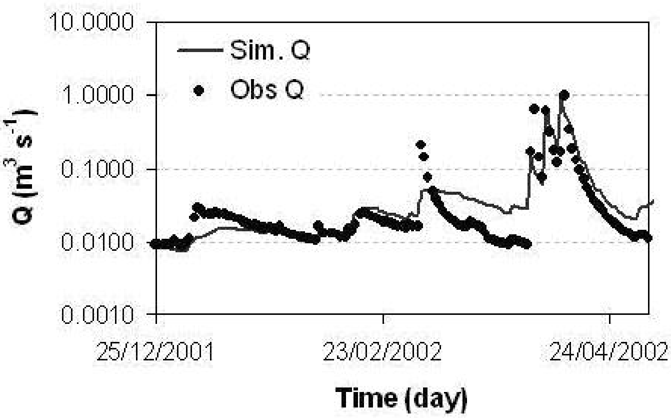
Observed nitrate and ammonium daily stream concentrations at Fuirosos and the corresponding simulated ones, obtained with the SD4-R-N model structure, are shown Fig. 5c.

The global discharge E index for the calibration period was 0.78, while for the first, second and third years respectively the E-index was 0.5, 0.4 and 0.86 (Table 2). The BE error was less than 8%. Concerning the nitrate simulation, the E index for the whole period was approximately 0.68 and the BE error less than -9% (Table 2).

Interestingly, this model structure could improve the simulation of the discharge peak flow observed on March 2002 (Fig. 9), which corresponded with the highest nitrate concentration peak observed during the calibration period (Fig. 5). This discharge event can be classified as 'intermediate flow' ($0.05\ m^3s^{-1} \leq Q < 1\ m^3\ s^{-1}$) according to Medici et al. (2008), which means that interflow was likely to have contributed along with the quick base flow. This suggestion is also supported by the slope steepness of the hydrograph recession. Neither the lumped LU4-N model nor the semi-distributed LU4-R-N model could reproduce this discharge event because no interflow was generated in that instance and the only flow contributing to the discharge was the quick base flow. This improvement was reflected by the SD4-N-R model's ability to simulate satisfactorily the corresponding nitrate peak concentration which resulted in an E index for the third year greater than 0.6 for the streamwater nitrate concentration simulations (Fig. 5c and Table 2).

Also in this case, the riparian zone was highlighted as a quite active zone where both the annual and daily M:N ratio were most of the time quite close to 1:1, as in the case of the LU4-R-N model (Fig. 6). The M:N ratio behaviour for the leucogranite and granodiorite units was quite similar to the one obtained with the LU4-R-N model for the so called hill-slope area, while in the scericitic schists unit the nitrification process could take place more easily than in the rest of the hill-slope giving in general smaller values for the M:N ratio (Fig. 4 and Fig. 10b).

a.



b.

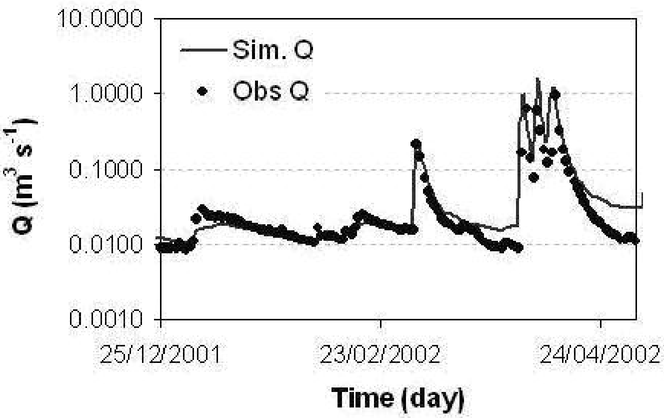


Fig. 9. Simulated and observed discharges (m^3 s^{-1}) for the event of March 2002 obtained with: a) the LU4-R-N model and b) the SD4-R-N model.

The sericitic unit is mainly facing North and it is largely covered by a deciduous woodland (chestnut (*Castanea sativa*), hazel (*Corylus avellana*) and oak (*Quercus pubescens*) with well-developed litter layers which could bring about higher nitrification rates than in the granitic units.

Finally, concerning the ammonium daily concentrations, the SD4-R-N model could not reproduce satisfactorily the daily NH_4 concentration for the calibration period (Fig. 5c, Table 2). The temporal validation results for this model structure are shown in Figure 7c and Table 3. The E index slightly decreased to 0.32. Also in this case, a simple one-at-a-time perturbation sensitivity analysis highlighted in general the mineralization related parameters as the most sensitive, as well as the maximum static storage water contents of each HRUs (H_u^*) and the annual maximum ammonium plant uptake ($MaxUP_{NH4}$). Moreover, also the ammonium soil adsorption rate (K_{ads}) and both hillslope and riparian zone nitrification soil moisture threshold (U_{nitr}) were highlighted as quite influential parameters especially considering the ammonium related objective functions.

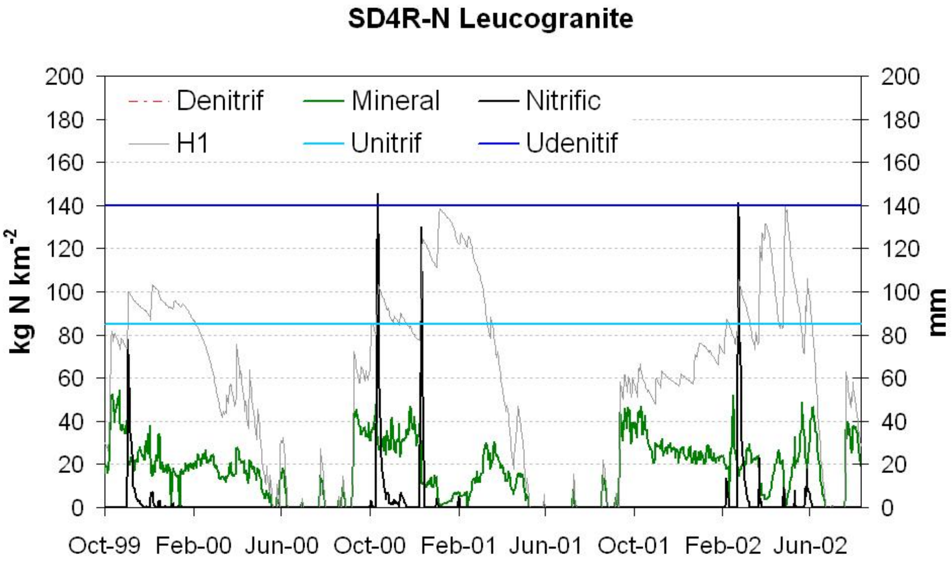


Fig. 10a. Simulated soil moisture content H_1 (grey line), nitrification soil moisture threshold U_{nitr}, light blue line and denitrification soil moisture threshold U_{denitr}, dark blue line in mm, plus simulated mineralization (green line), nitrification (black line) and denitrification (red line) daily loads (kg N km^{-2}) for the leucogranite lithologic unit (calibration period 1999-2002) with the SD4-R-N model.

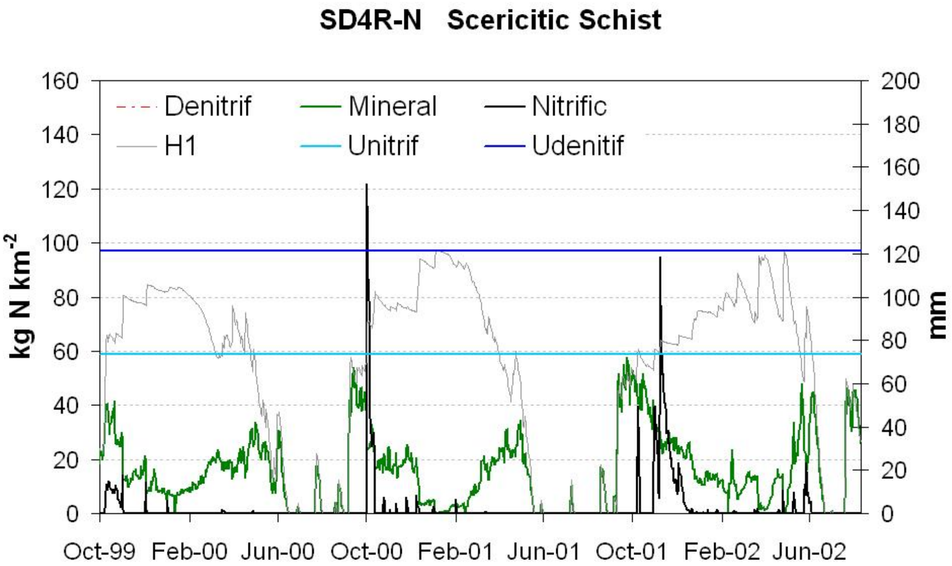


Fig. 10b. Simulated soil moisture content H_1 (grey line), nitrification soil moisture threshold U_{nitr}, light blue line and denitrification soil moisture threshold U_{denitr}, dark blue line in mm, plus simulated mineralization (green line), nitrification (black line) and denitrification (red line) daily loads (kg N km^{-2}) for the schist lithologic unit (calibration period 1999-2002) with the SD4-R-N model.

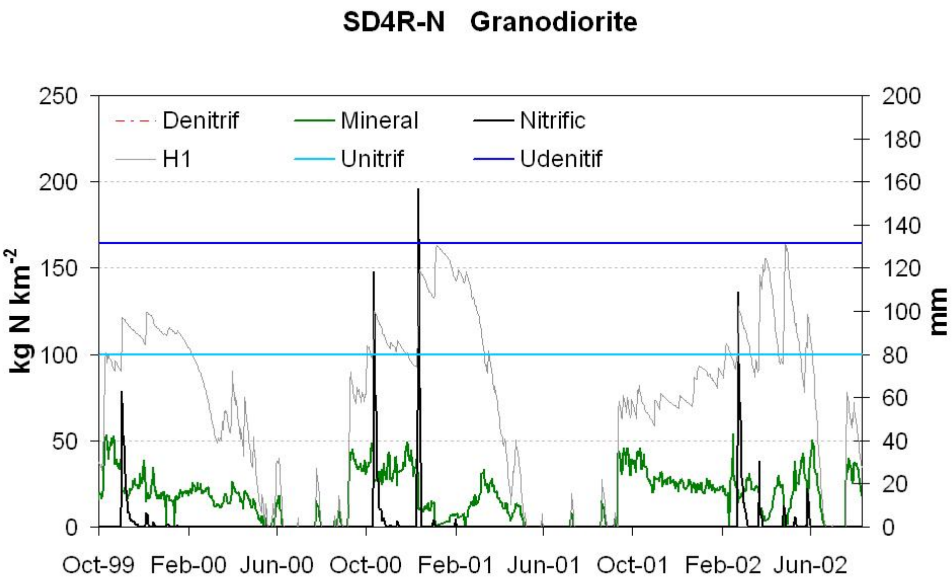


Fig. 10c. Simulated soil moisture content H_1 (grey line), nitrification soil moisture threshold U_{nitr}, light blue line and denitrification soil moisture threshold U_{denitr}, dark blue line in mm, plus simulated mineralization (green line), nitrification (black line) and denitrification (red line) daily loads (kg N km^{-2}) for the granodiorite lithologic unit (calibration period 1999-2002) with the SD4-R-N model.

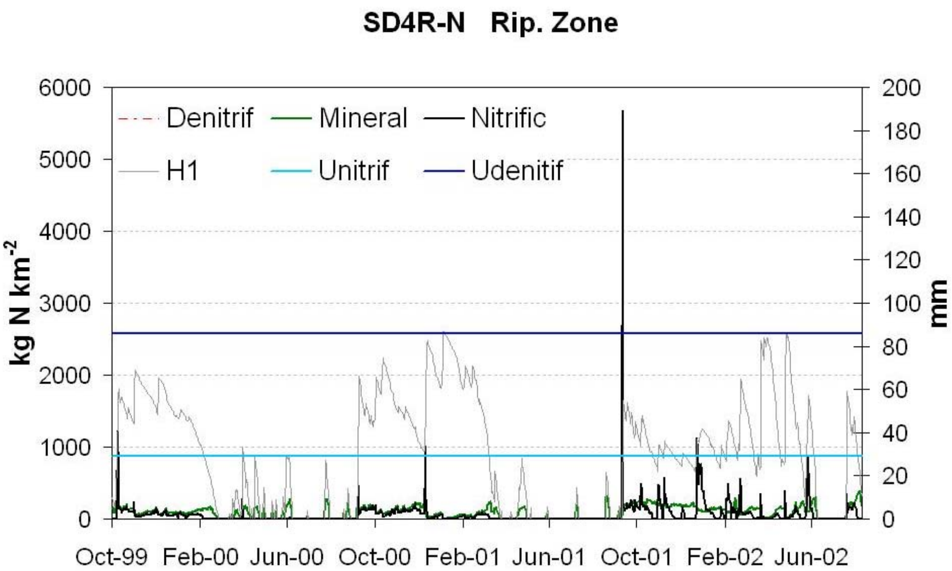


Fig. 10d. Simulated soil moisture content H_1 (grey line), nitrification soil moisture threshold U_{nitr}, light blue line and denitrification soil moisture threshold U_{denitr}, dark blue line in mm, plus simulated mineralization (green line), nitrification (black line) and denitrification (red line) daily loads (kg N km^{-2}) for the riparian zone (calibration period 1999-2002) with the SD4-R-N model.

4. Discussion

The LU4-N model performance for the calibration period could be considered satisfactory in terms of daily nitrate concentration. However, the temporal validation process calls for caution when considering the result obtained, even if one year for the validation may not be sufficient to accept or reject a model conceptualization. Inspection of the validation results pointed out that the LU4-N model simulated adequately the discharge event observed during March 2002 (Medici et al., 2008), but was unable to reproduce the associated nitrate peak. In fact, there was insufficient nitrate left in soil to be washed into the stream by the interflow to create a peak in the streamwater nitrate concentrations.

Lowering the nitrate plant uptake from 50 (day^{-1}) to 0.3 (day^{-1}), which would be the maximum rate allowed to increase stream nitrate concentration during the validation period, increased the BE error for the calibration period to approximately 169% without significantly improving the model validation performance (E remained negative and BE increased to 75%). Alternatively, the problem may be related to the nitrification dynamic; a more continuous nitrification process instead of a pulsed response could help to improve nitrate simulation during the validation period. However, problems arose when a permanently nitrification dynamic for the whole catchment was invoked. Specifically, it became impossible to simulate a M:N ratio consistent with the one observed by Serrasolses (1999), unless the nitrification rate was kept extremely low but this resulted in a failure to represent the observed nitrate peaks. Also when considering a high mineralization rate that caused extremely high stream ammonium concentration, the annual immobilization rate became largely beyond the range expected from literature values (i.e.: approximately 0.1 kg N ha^{-1} yr^{-1} according to Bonilla (1990), after Bernal et al., 2004).

The impossibility of obtaining acceptable results with the LU4-N model for the validation process forced us to explore different model structures. To this end, several authors (Butturini et al., 2003, Bernal et al, 2007, McIntyre et al., 2009) noted the importance of the riparian zone as a “hot spot” for nitrate removal/production in Mediterranean catchments. It was also highlighted that the mechanism of mineralization-nitrification can be essentially different from the rest of the catchment due to the specific moisture condition and different organic matter that can be found there. Therefore, it was thought the role played by the riparian zone should have been taken into account, even if it is well known that adding model components and parameters to reproduce specific aspects of catchment behaviour does not necessarily lead to better results.

Therefore, the lumped LU4-N model was evolved to a semi-distributed model that was applied considering firstly 2 HRUs (LU4-R-N) and then taking into account 4 HRUs (SD4-R-N), as previously explained.

According to the LU4-R-N and SD4-R-N models conceptualization, microbial processes in the hill-slope occur in pulses stimulated by soil moisture increasing after rain (Fig. 8 and Fig. 9), as it was for the whole catchment with the LU4-N model (Fig. 4). Namely, simulated nitrification, immobilisation and denitrification were allowed to occur only after exceeding their respective soil moisture thresholds (Table 1). This threshold mechanism gives rise in the hill-slope to pulses that are particularly significant for nitrification.

The LU4-R-N and SD4-R-N models, due to the threshold mechanism, reproduced in the hill-slope soil an annual average M:N ratio of approximately 8:1, which is consistent with the ratio (10:1) founded in other Mediterranean areas (e.g., Serrasolses et al., 1999), which was explained considering soil moisture limitation of nitrification. Interestingly, when considering the riparian zone alone the simulated M:N ratio decreased in both cases to almost 1:1 (Fig. 6). Supporting our simulations, Merrill (2006) found out that measured net mineralisation and net nitrification rates were similar in riparian zone ecosystem types. Moreover, it was found that in four of the five ecosystems considered in the study by Merrill (2006), net mineralization rates explained over 60% of the variation in net nitrification.

This specific behaviour of the riparian soil allowed to easily accumulating nitrate that could be washed away by the interflow derived from the hill-slope causing significant increase in nitrate streamwater concentrations. Butturini et al. (2003) previously pointed out the unsaturated riparian soil layer at Fuirosos as a possible source of nitrate. In this study, it was observed that the rise of the local riparian groundwater table, after the summer drought, resulted in the rapid flushing of nitrate stored in the soil during the long dry period. Our results suggested also a higher mineralization rate in the riparian area than in the rest of the catchment. A possible explanation for that, may be that the major tree species at the hill-slope of Fuirosos are perennial cork oak (*Quercus suber*) and pine (*Pinus halepensis* and *Pinus pinaster*), therefore the mineralization rates are expected to be low as a consequence of allelopathic compounds leached from plants and the quality of sclerophyllous leaf (Gallardo and Merino, 1992; Castaldi et al., 2002). The stream channel is flanked by a well-developed riparian area where alder *(Alnus glutionosa*) – a tree species with high quality litter, and exotic plane tree (*Platanus acerifolia*) predominates, allowing for higher decomposition and mineralization rates of litter accumulated on the stream bed and stream edge zone. Moreover, Acuña et al. (2007) observed that in the Fuirosos stream, leaf fall may extend from late summer to autumn (August to November) during dry years, due to hydrologic stress. Therefore, large inputs of organic matter accumulating on the streambed and riparian zone may fuel heterotrophic activity during the transition and wet periods (Von Schiller et al. 2008). Simulated mineralization was highest immediately after the summer drought period, when the soil moisture content was approximately 50% or less of the maximum soil static water content. This is consistent with the study of McIntyre et al. (2009) which noted that, for a semi-arid intermittent stream, mineralization would be reduced under soil moisture conditions close to saturation, while it would increase under moderate saturation. Other authors observed a high rate of humus decomposition and rapid mineralization following rewetting of dry soils and it was also observed that soils subject to wetting and drying cycles, release more nitrogen than continuously moist soil (Birch, 1964, Dick et al, 2005, Rey et al., 2005). Bernal et al. (2005) observed, at Fuirosos, that mineralization activity existed in the mineral soil and/or in the stream channel particularly during the transition period from dry to wet conditions and in a previous study performed in the soil of the riparian area of Fuirosos, Bernal et al. (2003) reported the highest mineralization rates in autumn.

Interestingly, the SD4-R-N model reproduced a huge pulse of nitrification in the riparian soil just after the summer drought 2001 because of a sudden increase in soil moisture content due to the reverse flux (that is water flowing from the stream to the riparian zone), which is characteristic of arid and semi-arid areas (Fig. 9). This is consistent with Butturini et al. (2003) that pointed out the reverse flux as a possible mechanism responsible for nitrate release in the riparian zone.

All the model structures considered included denitrification and nitrification in the shallow aquifer. This was necessary to represent the nitrate behaviour. These processes controlled the rate of reduction in the streamwater nitrate and ammonium concentrations during base flow conditions. This is consistent with previous studies of biogeochemical activities in the unsaturated zone of weathered granite (Legout et al., 2005) which demonstrated potential for bacterial activity and biogeochemical reaction in the lower soil horizons associated with lower carbon content. In particular, Legout et al. (2005) suggested that both nitrification and denitrification are likely to take place in the unsaturated weathered granite below the soil organic horizon. The denitrification process occurring in the riparian groundwater was especially relevant for the SD4-R-N model (Fig. 11), while for the LU4-R-N model denitrification occurred mainly in the riparian upper soil (Fig. 8). In our model the riparian interflow eventually percolates to the local riparian aquifer due to the extremely low slope in this catchment area and thus, it is nearly impossible to distinguish between soil and aquifer riparian denitrification (Fig. 3). Nonetheless, our results highlighted that the denitrification process in the riparian zone is a key mechanism to the reduction of groundwater nitrate in particular during the wettest period of the year. This is consistent with previous studies in Mediterranean areas (Peterjohn and Correl 1984, Butturini et al., 2003, Rassam et al., 2006 and Bernal et al. 2007).

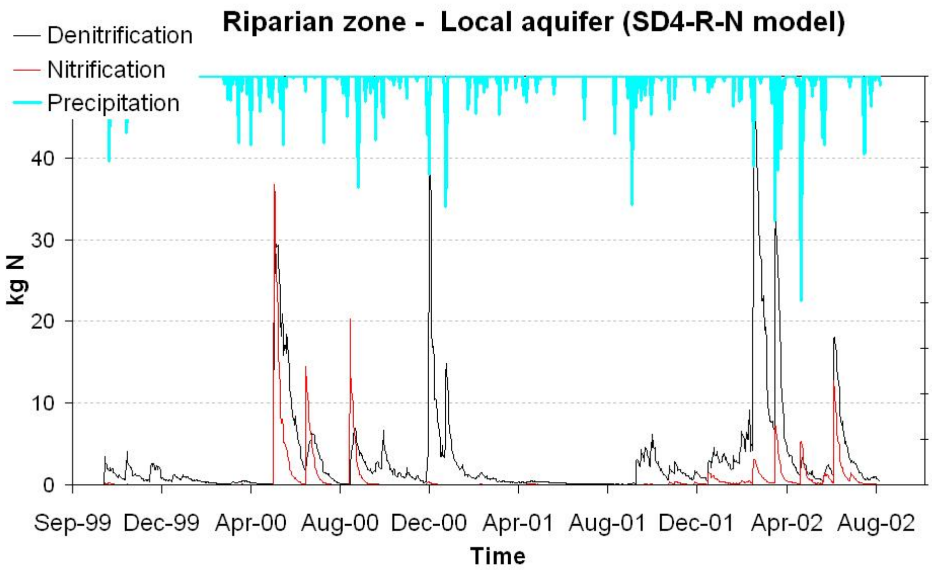


Figure 11. Simulated denitrification process (kg N) in the riparian local aquifer with the LU4-R-N and SD4-R-N models.

Finally, none of the considered models could reproduce satisfactorily the daily stream ammonium concentration, which was low even during precipitation events. The observed stream daily ammonium concentration presents extremely low values, which do not increase even during precipitation events. In annual terms, the relative contribution of nitrogen forms to the total catchment annual export is 57%, 35% and 8% as NO_3-N, DON and NH_4-N respectively (Bernal et al., 2005). Moreover, the standard deviation of the chemical water analysis procedure adopted is approximately 0.02 mg N/l (Hach Company, 1992. Water Analysis Handbook, 2nd ed. Hach Company, Loveland, Co.), which has the same magnitude of most observed daily ammonium concentrations. Thus, low ammonium concentrations which are not linked to flow as strongly as for nitrate are difficult to simulate satisfactorily. Nevertheless, the models could represent at least the ammonium general trend and order of magnitude, which taking into account its erratic behaviour it can be considered an acceptable result. In particular, differently from the INCA-N model, they did not simulate ammonium leaching during storm flow because we included the adsorption/desorption mechanism in the soil compartment improving its simulation.

5. Conclusions

The aim of this study was to improve our understanding of the main processes that govern the inorganic nitrogen fate and losses in Mediterranean catchments by means of mathematical modelling. The results highlighted that in those ecosystems a pulse dynamic for most of the soil biological processes, related with the rainfall pattern occurs as previously suggested by Schiwinning (2004b). We reproduced this pulse dynamic by introducing a moisture threshold for each simulated soil-biological process. The concept of response thresholds is recurrent in the ecology of arid/semi-arid systems (Beatly 1974), and it has been used to explain the decoupling of nutrient gain and losses mechanisms (Schwinninng et al., 2004b). Our simulations suggested that nitrification shows a pulse dynamic in the hillslope soil, while it occurs more continuously in the riparian soil, which together with the interflow flushing effect can give rise to important stream nitrate concentration peaks during some periods of the year.
These results point towards the riparian upper soil as a possible source of nitrate in this type of ecosystems, consistently with that observed in

previous empirical studies (e.g., Butturini et al. 2003). Interestingly, the model reproduced by means of calibration the so-called “Birch effect”, which implies higher mineralization rate just after the summer drought. Finally, the results indicate the importance of the nitrification and denitrification processes in the unsaturated weathered granite below the soil organic horizon.

The LU4-R-N and the SD4-R-N semi-distributed models could be calibrated to simulate flow and nitrate dynamic in Fuirosos and gave acceptable result for the temporal validation process. This suggests that the key processes controlling flow and nitrate behaviour are included within these models conceptual schemes and their mathematical representation seems reasonable.

Table 4. Nitrogen annual process rates

N Processes	Measured values [Kg N ha^{-1} day^{-1}]*	Sim. values [Kg N ha^{-1} day^{-1}] LU4-N	Sim. values [Kg N ha^{-1} day^{-1}] LU4R-N	Sim. values [Kg N ha^{-1} day^{-1}] SD4R-N
Net mineralization	32.4 – 80.1	62.9	64.18	61.94
Net nitrification	4.4 – 7.5	6.19	7.83	8.84
Immobilization	0.08	4.8	4.52	0.08
Nitrate uptake by vegetation	10.3 - 58	13.42	13.51	14.94
Ammonium uptake by vegetation	53 – 80.5	59.17	58.79	60.67

*After Bernal et al., 2004

Further work is needed to develop better simulations of ammonium storage and transport in the catchment and the link between organic-N and ammonium. In particular, a better understanding of the forms and quantities of organic-N is required. The three models described in the paper take into account the mineralization process in a very simplified way, considering the organic matter as unlimited and without distinguishing among different kind of organic matter, which may have certain influence on the ammonium simulation results. It is known that the mass of ammonium is influenced by organic matter temporal variability and availability. However, a more complex description of this key process might increase dramatically the parameters to be calibrated introducing more uncertainty into the model. Finally, it has to be highlighted that the models developed do not include any in-stream processes yet, which may be important in controlling the instream ammonium concentrations (von Schiller D., et al. 2008).

Acknowledgements

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4.3

*Sensitivity analysis of three N-models of varying complexity applied in a small Mediterranean forested catchment**

Key words

General Sensitivity Analysis; GLUE framework

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1. Introduction

Mathematical models have been developed to describe nitrogen dynamics in catchments, however there is a substantial gap between the outputs now expected from these models in terms of spatial and temporal resolution and what modellers are able to provide with scientific justification (McIntyre et al., 2005). Process-based models are often complex because they aim to describe all the main factors and processes in order to understand the relative importance of these and test their response to environmental change (Dean et al., 2009). Mediterranean catchments are particularly complex systems due to their characteristic high inter and intra-annual variability in flow (Gallart et al., 2002) and the influence that wet-dry cycles have on biological processes, as stressed by many authors (Peterjohn and Schlesinger 1991; Van Gestel et al., 1993; Mummey et al., 1994). A more realistic representation of real-world thresholds and nonlinearities motivates the use of complex models with high numbers of parameters, in some cases more than one hundred, and it also encourages the consequent need for more rigorous evaluations of model performance (Wagener et al., 2007). However, models will always necessarily be simplification of reality; hence, models parameters have to be understood as "effective" parameters that compensate for the underlying variability in processes, site characteristics and input errors (Beven, 2001; Mertens et al., 2005; Francés et al., 2007). The effective parameters values for a particular model structure will then need to be calibrated in some way. Beven (2001) highlights that many models and many parameter combinations give equally good fits to data, indicating that is impossible to find an optimal model or an optimal parameter set in hydrological modelling. This was called by Beven 'equifinality problem' (even if the original concept defined by Karl Ludwig von Bertalanffy is slightly different: *'Equifinality is the principle that in open systems a given end state can be reached by many potential means'*). Thus, such models have been described as mathematical marionettes which '…often can dance to the tune of the calibration data' (Kirchner, 2006). All model calibrations and subsequent predictions are subject to uncertainty (Seibert, 2003) and the assessment of this issue in water quality modelling is increasingly appreciated (Kruger et al., 2007; Rode et al., 2007; Dean et al., 2009). To this end, sensitivity analysis provides an evaluation of a model's robustness, giving information regarding the effect of model parameters and input data on the resultant model output. This analysis often leads to improvements in the mathematical model: by removal of insensitive parameters; by targeted acquisition of further data to provide information on a particular process; and by refinement of the underlying perceptual model. Such analysis can show where knowledge gaps are most severe and which of the model parameters or aspects of the model structure most strongly affect prediction uncertainty (Wagener et al., 2003 and 2007). In this paper, a general sensitivity analysis (GSA) using Monte Carlo simulations (Hornberger and Spear, 1980) and the Generalized Likelihood Uncertainty Estimation (GLUE) methodology (Beven and Binley, 1992) was done to three catchment-scale nitrogen models of varying complexity when applied to a small Mediterranean forested catchment, the Fuirosos, located in the north-east of Spain (Medici et al., 2008 and Medici et al., 2010). Specifically the aim of the work is to determine if additional model complexity gives a better capability to model the hydrology and nitrogen dynamics of the Fuirosos catchment. To address this, there are two research questions: (1) do the results show that additional model complexity actually gives more acceptable model behaviours? (2) does a more complex model structure leads to fewer model fits, suggesting that the problem of equifinality may not be so severe in case of water quality modelling?

The first research questions is related to the principle of parsimony (William of Ockham, 14th-century), which requires models to have the simplest parameterization that can be used to represent the data. However, careful consideration is required to ensure that model does not omit one or more processes important for a particular problem. In fact, a model with a simple structure often does not make the best use of the available data and can be unreliable outside the range of catchment conditions on which it was calibrated (Kuczera and Mroczkowski, 1998). The model structure and the model parameters cannot be identified properly if there are too many models parameters and insufficient data to test the model performance (Rankinen et al. 2006).

2. Model application and development

Three catchment-scale hydrology and nitrogen models were developed to simulate the flows and streamwater inorganic nitrogen dynamics in the Fuirosos catchment. The three models increased in their spatial complexity evolving from an initial lumped structure (LU4-N) to a semi-distributed one (LU4-R-N) that included the riparian zone along with the four small reservoirs of the catchment represented to a more complex semi-distributed one (SD4-R-N) that included the riparian zone, the four reservoirs as well as catchment spatial variability in land cover and geology (Bernal et al., 2004, Medici et al., 2008; Medici et al., 2010). The progression from the simplest conceptual model to the most complex is reflected by an increase in the number of parameters from 27 to 59.

The three process-based models simulate water discharge and stream nitrate and ammonium concentrations at daily time step. The LU4-N model is a lumped model that describes the Fuirosos catchment as homogeneous and represents the simplest conceptualization adopted; it is characterized by 27 parameters that require calibration (of which 8 are for the rainfall-runoff sub-model and 19 for the nitrogen sub-model). The LU4-N model was evolved to a semi-distributed model, LU4-R-N, which includes 41 parameters requiring calibration (of which 10 are for the rainfall-runoff component of the model and 31 for the nitrogen sub-model). The LU4-R-N model was then evolved to a more complex semi-distributed model, SD4-R-N, that includes 59 parameters to be optimized (of which 28 for the rainfall-runoff component and 31 for the nitrogen sub-model). The main difference between the semi-distributed models (LU4-R-N and SD4-R-N) and the lumped model (LU4-N) is that the two semi-distributed models simulate water movement and inorganic nitrogen dynamics in the riparian zone, which was introduced to represent successfully the catchment drying-up period and the non-linear hydrological behaviour during the wetting-up period (Medici et al. 2008 and 2010). The riparian zone was also identified as a possible source of nitrate that entered the streamwater, especially after the summer drought period and as an important nitrate sink (due to denitrification) during winter/spring, the wettest period of the year (Butturini et al., 2002; Bernal et al. 2008; Medici et al., 2010).

All three models include soil moisture thresholds, introduced to reproduce the nonlinearities observed in the hydrological and nitrogen behaviour. For example, concerning the hydrology, a soil moisture threshold was defined as a percentage of the maximum static storage capacity (considering only the water retained by soil capillary forces). In this way, the deep percolation can recharge the permanently saturated zone only during the wet period when the soil water content exceeds the aforementioned soil moisture threshold. During the rest of the year, a shallow perched water table occurs in the upper part of the weathered bedrock. The nitrogen sub-model includes biological thresholds that respond to increased soil moisture to deliver pulses of nitrate and ammonium to the streamwaters. Such pulses are observed in Mediterranean and semi-arid environments (Schiwinning et al., 2004a and 2004b).

3. Sensitivity analysis methodology

A general sensitivity analysis (GSA) was done to identify the key model parameters controlling the flow and nitrogen behaviour at Fuirosos. The GSA method was that developed and applied by Hornberger and Spear (1980) and Whitehead and Young (1979). Random sampling of parameters values from uniform distributions was done, so that each parameter value had an equal chance of being chosen as part of a Monte-Carlo procedure whereby 100,000 input parameters sets were sampled independently from the user-defined ranges specified in Table 1. The ranges were specified using *a priori* knowledge and previous calibration and testing (Medici et al., 2008 and 2010). Due to a lack of data with which to specify the initial soil available water and the soil, groundwater and streamwater nitrate and ammonium concentrations, then these initial conditions were also included in the GSA. Though when a warm-up period of one month (from 13/10/1999 to 13/11/1999), it was found that the initial conditions did not show any significant influence on the discharge and nitrogen simulation, hence they were removed from the sensitivity analysis to reduce the number of parameters simultaneously analyzed compared to the feasible number of Monte Carlo simulations.

For each model run the flow and streamwater nitrate and ammonium concentrations were obtained and the objective functions calculated. Based on these calculations the modelled output was identified as either representative (hereafter behavioural) or not representative (non-behavioural) of the generalized behavioural criteria, defined as follows. The objective functions used were the Nash and Sutcliffe efficiency index (E) and the Relative Root Mean Squared Error (RRMSE) as defined by Franchello et al., (2004). This second coefficient was taken into account due to the ammonium E efficiency index being almost always negative. Both these coefficients are biased towards fitting high values of discharge and concentration because they are based on square error. The E efficiency index was calculated for the whole calibration period (then named E_{tot}) and for each year individually (then named $E_{1yr,}$ E_{2yr} and E_{3yr}) the sum of which ($E_{123} = E_{1yr} + E_{2yr} + E_{3yr}$) was also used as an additional objective function. The thresholds of acceptability for discharge were set at $E_{tot}(Q) \geq 0.77$ or $RRMSE(Q) \leq 0.5$ and at $E_{123}(Q) \geq 1.5$ plus $E_{1yr,}$ E_{2yr} and $E_{3yr} \geq 0.5$ simultaneously (hereafter indicated as E^{*}_{123} when the additional condition on each annual E is considered). It is worth to highlight that these three hydrological years were characterised by a large variability in river flow and climatic conditions, as outlined in the section 2. Therefore, the last behavioural criteria lead indirectly to make an effort to reproduce different hydrograph characteristics at the same time, as the baseflow (focusing on the first year, the driest one) or discharge peaks (focusing on the third year, the wettest one). Therefore, hereafter E^*_{123} will be mentioned as multi-objective approach, where each one of the three years has the same weight.

For the nitrogen simulation the thresholds of acceptability were set at RRMSE(NO_3)≤0.6 and RRMSE(NH_4)≤1.2 plus the five criteria shown in Table 2, as previously done by Wade et al. (2001).

Each simulation result consisted of the parameter vector itself and the behavioural outcome (i.e. the value of the objective function considered). The final result of the 100,000 simulations is *m* parameter vectors that led to behaviour and *n* = (100,000-*m*) which did not.

Table 1: Analysed parameters with initial range

Parameter name	Unit	Min. bound	Max. bound
H1i – Initial soil water content	mm	0.00	50.00
H2i – Initial surface water content	mm	0.00	1.00
H3i – Initial gravitational water content	mm	0.00	5.00
H4i – Initial shallow aquifer water content	mm	0.00	10.00
H5i – Initial deeper aquifer water content	mm	0.00	20.00
NH_4Ads_i – Initial adsorbed soil ammonium	kg N km^{-2}	0.00	4.00
NH_4Deep_i – Initial deep aquifer ammonium	Kg N km^{-2}	0.00	4.00
NO_3Soil_i – Initial soil nitrate	kg N km^{-2}	0.00	12.00
$NH_4Shallow_i$ – Initial shallow aq. ammonium	kg N km^{-2}	0.00	8.00
NO_3Deep_i – Initial deep aquifer nitrate	kg N km^{-2}	0.00	5.00
$NO_3Shallow_i$ – Initial shallow aquifer nitrate	kg N km^{-2}	0.00	5.00
NH_4Soil_i – Initial soil ammonium	kg N km^{-2}	0.00	5.00
Hu max – Max. static storage water content	mm	100.00	200.00
Hu max ripz – Riparian Max. static st. water cont.	mm	60	110
Ks – Surface infiltration capacity	mm	15.00	40.00
Ks ripz– Riparian surface infiltration capacity	mm	4.00	18.00
Kp – Percolation capacity to shallow aquifer	mm	4.00	18.00
Kpp – Percolation capacity to deeper aquifer	mm	1.00	14.00
T2 – Upper gravit. Storage residence time	day	1.30	3.00
T3 – Shallow aquifer residence time	day	15.00	40.00
T4 – Deeper aquifer residence time	day	2000	3500
H_m - Threshold for deep percolation	mm	40.00	150.00
Kmin – Mineralization rate constant	kg N $ha^{-1}day^{-1}$	0.45	0.60
Kmin ripz – Riparian miner. rate constant	kg N $ha^{-1}day^{-1}$	3.0	4.0
Knitr – Nitrification rate constant	day^{-1}	0.30	2.0
Knitr ripz – Riparian nitrification rate constant	day^{-1}	0.30	2.5
Kimm – Immobilization rate constant	day^{-1}	0.00	0.70
Kimm ripz – Rip. iImmobilization rate constant	day^{-1}	0.00	0.70
Kdenitr – Soil denitrification rate constant	day^{-1}	0.01	0.15
Kdenitr ripz – Rip. soil denitrify. rate constant	day^{-1}	1.0	2.0
Kdenitr_aquif – Shallow aq. denitr. Rate const.	day^{-1}	0.02	0.35
Kdenitr_aquif ripz – Rip. shallow aq. denitr. rate c.	day^{-1}	0.02	0.35
Knitr_aquif – Shallow aq. nitr. rate const.	day^{-1}	0.1	2.60
Knitr_aquif rip– Rip. shallow aq. nitr. rate const.	day^{-1}	0.1	2.60
Kads – Adsortion rate constant	day^{-1}	0.7	0.97
Kdes – Desorption rate constant	day^{-1}	0.03	0.70
$KupNH_4$ / $KupNH_4$ ripz. – Ammonium plant uptake rate c.	day^{-1}	1.00	80.00
$KupNO_3$ / $KupNO_3$ ripz.– Nitrate plant uptake rate c.	day^{-1}	1.00	80.00
Udenitr – Soil denitrification threshold	%	55.00	100.00
Udenitr ripz. – Rip. soil denitrify. threshold	%	55.00	100.00
Uimmob – Soil immobilization threshold	%	35.00	100.00
Uimmob ripz – Rip. soil immobilization threshold	%	35.00	100.00
Umin – Soil mineralization threshold	%	40.00	58.00

Umin ripz. – Rip. soil mineralization threshold		20.00	45.00
Unitr – Soil nitrification threshold	%	47.00	65.00
Unitr ripz. – Rip. soil nitrification threshold	%	30.00	45.00
$MaxAdsNH_4$ – Max daily ads. Ammonium	kg N $ha^{-1}yr^{-1}$	10.00	50.00
$MaxUPNH_4$ – Max ammonium uptake	kg N $ha^{-1}yr^{-1}$	80.00	110.00
$MaxUPNO_3$ – Max nitrate uptake	kg N $ha^{-1}yr^{-1}$	50.00	120.00
$WMaxUPNO_3$ – Max nitrate uptake in winter	kg N $ha^{-1}yr^{-1}$	10.00	25.00
C_9 – Max temperature difference	ºC	5.50	7.5

The final results were analyzed to identify the key parameters causing the models to reproduce the observed behaviour. Specifically, the cumulative probability distribution for *m* behaviours and *n* non-behaviours were calculated and a Kolmogorov-Smirnov two-sample test (KS) was used to assess the separation between the two cumulative probability distributions for each model parameter (Hornberger and Spear, 1980). The statistic KS is determined as the maximum vertical distance between the cumulative probability distribution curves and statistically significant values of KS indicate that a parameter is important for simulating behaviour. The significant parameters were ranked in importance based on the KS values. This statistic has been previously used in this manner by Wade et al., (2001) and McIntyre et al., (2005). An extension of the GSA proposed by Spear and Hornberger (1980) is the generalized likelihood uncertainty estimation (GLUE) methodology that provides with additional information on models behaviour. This methodology has been extensively explained in Beven and Binley (1992), Beven and Freer (2001) and Beven (2006 and 2008). GLUE also uses a performance measure threshold to define acceptable models, but instead of treating all acceptable models equally to look at global sensitivities as in the case of GSA, GLUE calculates a likelihood weight for each simulation (which can be seen as the associated degree of belief) by evaluating the performance of the simulation in comparison with observed data and then uses those weights to evaluate the 5% and 95% GLUE bounds over all the simulations considered acceptable (Dean et al., 2009).

Table 2: Nitrogen annual process rates: a comparison of values from previous studies in forests of Quercus ilex in Catalonia (Spain) with simulated values for the periods 1999-2000

N processes	**Measured values***
	kg N ha^{-1} $year^{-1}$
Net Mineralization	32.4 – 80.1
Net Nitrification	4.4 – 7.5
Immobilisation	0.08
Nitrate uptake by vegetation	10.3 - 58
Ammonium uptake by vegetation	53 – 80.5

*After Bernal et al., 2004

4. Results

4.1 LU4-N model sensitivity analysis

The first stage of this analysis considers the lumped LU4-N model and therefore focuses on identifying important model parameters and a general analysis of flow and nitrate. This is the simplest structure taken into account to model water discharge and inorganic nitrogen at Fuirosos. The total number of parameters being varied together was 27 (Table 1) and the 100,000 Monte Carlo simulations produced approximately 39,557 behavioural outputs considering RRMSE(Q) and 22,639 considering E_{tot}(Q). Table 3 (columns 2 and 3) lists the sensitivity ranking obtained in both cases. Both objective functions gave the same results in terms of model sensitivity to the parameters and the results give a clear indication that the hydrological model is greatly affected by the maximum static storage water content (H_{u_max}), which defines the maximum amount of water that can be held in the vegetation canopy, puddles and the upper soil due to capillary forces and adsorption (Medici et al., 2008). This water can leave the catchment only by evapotranspiration and therefore does not contribute to the modelled runoff. Surface infiltration capacity (K_s) and the threshold for deep percolation (H_m) are also important. The result concerning H_m is particularly interesting since it supports the introduction of the non-linear deep percolation mechanism (Medici et al., 2008), which was essential to reproduce the observed non-linear response after the summer drought and during the wet period of this small Mediterranean catchment. Figure 2 shows the $E_{tot}(Q)$ index plotted against the four most flow-significant parameters. This figure allows the identification of the 'optimum' parameter value to be visualised, which is far away from the expert calibration result (Medici et al., 2008 and 2010). Figure 2a also shows that the best Monte Carlo behavioural parameter set (depicted in Fig. 2 as a triangle) cannot reproduce the first hydrological year, the driest one (the E_{1yr} is negative and is not plotted on Fig. 2a). Whereas, the expert calibration parameters set gave a smaller value of $E_{tot}(Q)$ but could reproduce satisfactorily all the three different hydrological years (with annual E indexes greater than 0.6).

Table 3: Sensitivity ranking of LU4-N model parameters based on KS statistic

	LU4-N model			
Parameter name	**RRMSE(Q)≤0.5**	**E_{tot}(Q)≥0.77**	**E^*_{123}(Q)≥1.5**	**RRMSE(NO3)≤0.8 RRMSE(NH4)≤1.4**
Hu max	1 (0.731)	1 (0.729)	1 (0.537)	3 (0.295)
Ks	2 (0.256)	2 (0.270)	7 (0.024)	
Kp	4 (0.062)	4 (0.067)	6 (0.029)	9 (0.121)
Kpp			3 (0.151)	16 (0.054)
T2	5 (0.056)	5 (0.056)	5 (0.036)	
T3	6 (0.042)	6 (0.047)	4 (0.059)	
T4				
H_m	3 (0.181)	3 (0.215)	2 (0.372)	6 (0.212)
Kmin				2 (0.298)
Knitr				13 (0.086)
Kimm				14 (0.071)
Kdenitr				
Kdenitr_aquif				12 (0.092)
Knitr_aquif				1 (0.390)
Kads				10 (0.106)
Kdes				
$KupNH_4$				17 (0.049)
$KupNO_3$				11 (0.099)
Udenitr				
Uimmob				8 (0.122)
Umin				5 (0.227)
Unitr				7 (0.199)
$MaxAdsNH_4$				15 (0.059)
$MaxUPNH_4$				4 (0.278)
$MaxUPNO_3$				
$WMaxUPNO_3$				
C_9				

The same analysis based on the KS statistic, was repeated considering the multi-objective function E^*_{123}(Q). In this case, the number of behavioural simulations decreased to approximately 14,283 from 100,000 model runs. This second analysis provided a slightly different sensitivity ranking compared to that obtained considering just one objective function (Table 3, columns 2 and 3 compared to column 4). In this case, the parameter H_{u_max} was also the most influential one and all the base-flow related parameters gained importance and became more sensitive. For example, the percolation capacity to the deeper aquifer, K_{pp} became the third most influent parameter and the shallow aquifer residence time, T_3, became the fourth most influential parameter.

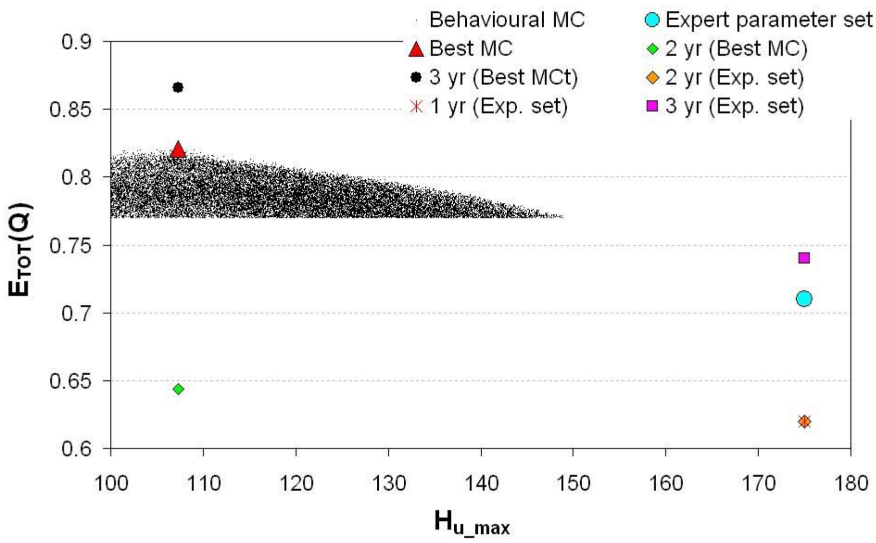


Fig. 2: Scatter plots of the four most flow significant parameters (model LU4-N) against $E_{tot}(Q)$ for the whole calibration period (99-02). The blue circle represents the expert calibration parameter set, while the red triangle represents the best $E_{tot}(Q)$ behavioural parameter set; a) H_{u_max}

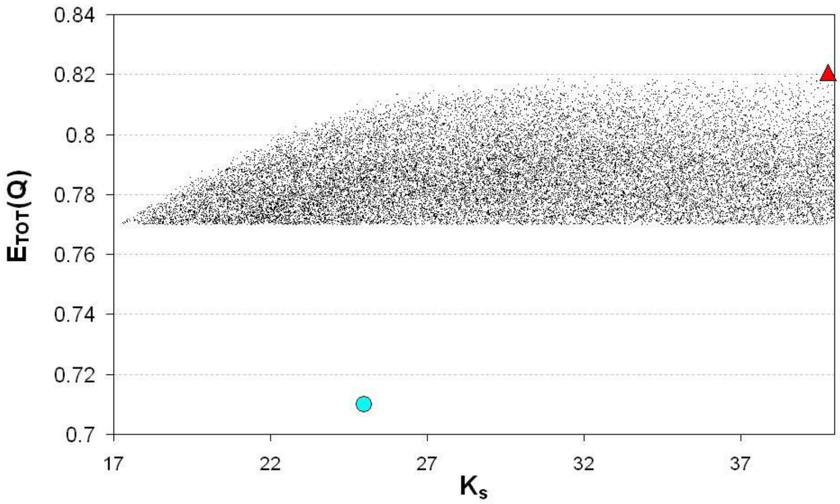


Fig. 2: Continuation b) K_s

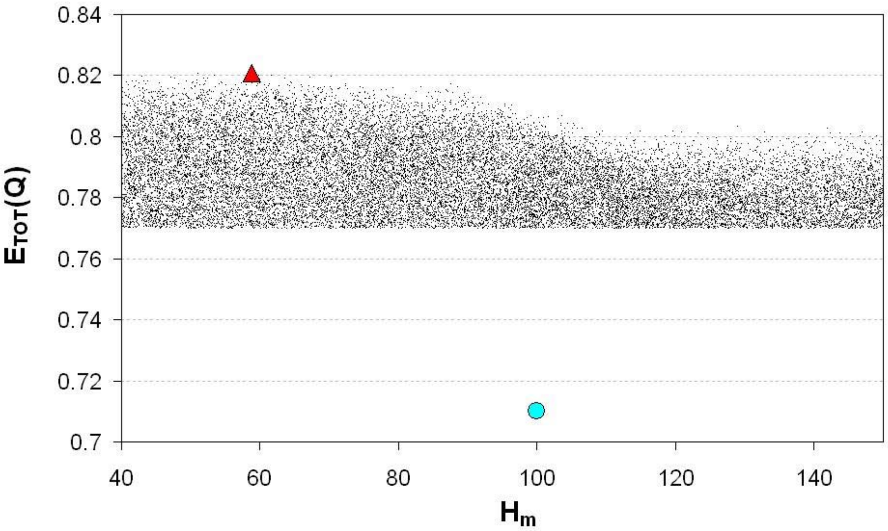


Fig. 2: Continuation c) H_m

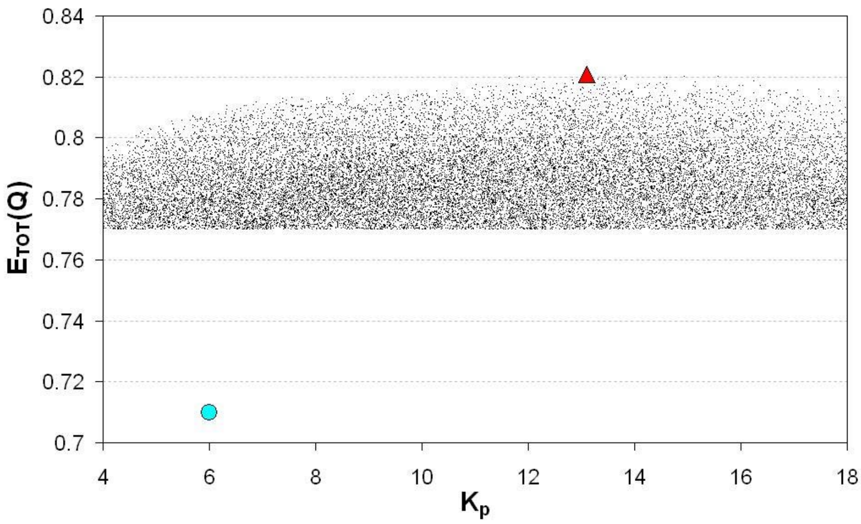


Fig. 2: Continuation d) K_p

Figure 3 shows the scatter plot of the four most sensitive parameters against each annual E index ($E_{1yr,}$ E_{2yr} and E_{3yr}) as well as $E_{tot}(Q)$. In this figure, the triangle represents the parameter set that led to the highest value of $E_{123}(Q)$; the yellow rhombus represent the near-optimum parameters sets for $E^{*}_{123}(Q)$. Figure 3 highlights that the near-optimum parameters space for $E^{*}_{123}(Q)$, namely where $E_{1yr,}$ E_{2yr} and E_{3yr} are equals or greater than 0.65, includes the expert parameters set (represented by the black point). The expert parameter set was obtained making an effort to fit the simulation to the shape of the hydrograph recession curves and the levels of baseflow, as well as to the peaks. Therefore, considering the expert parameter set as a good reference, it can be said that the multi-objective approach $E^{*}_{123}(Q)$ helps to constrain the variation range of the most sensitive parameters. For example, according to $E^{*}_{123}(Q)$ the parameter value of H_{u_max} tends to shift closer to the upper limit of its variation range (200 mm) than to the lower one. The single objective approach would lead to a much smaller value for H_{u_max}.

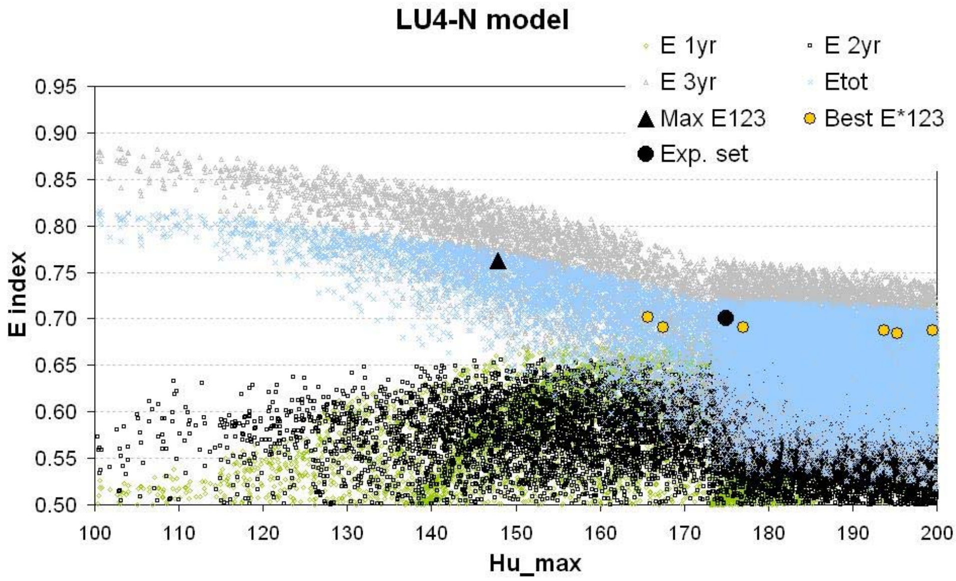


Fig. 3: Scatter plots of the four most significant parameters (LU4-N model) considering the multi-objective approach E^{*}_{123}. The black point representing the expert calibration; the triangle representing the best E_{123} behavioural parameter set and finally the yellow circles representing the near optimum parameters sets according to the multi-objective approach E^{*}_{123}; a) H_{u_max} parameter

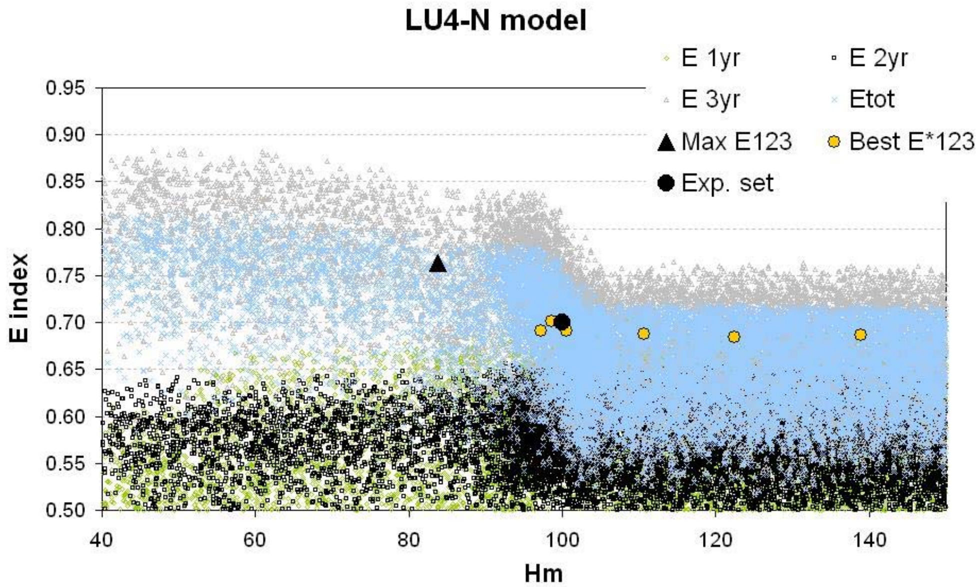


Fig. 3: Continuation; b) H_m

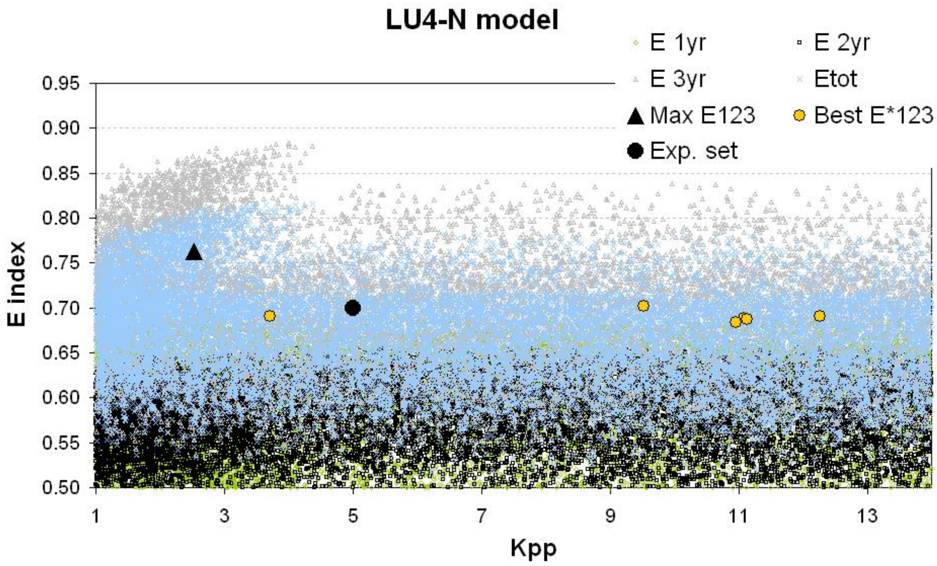


Fig. 3: Continuation; c) K_{pp} parameter

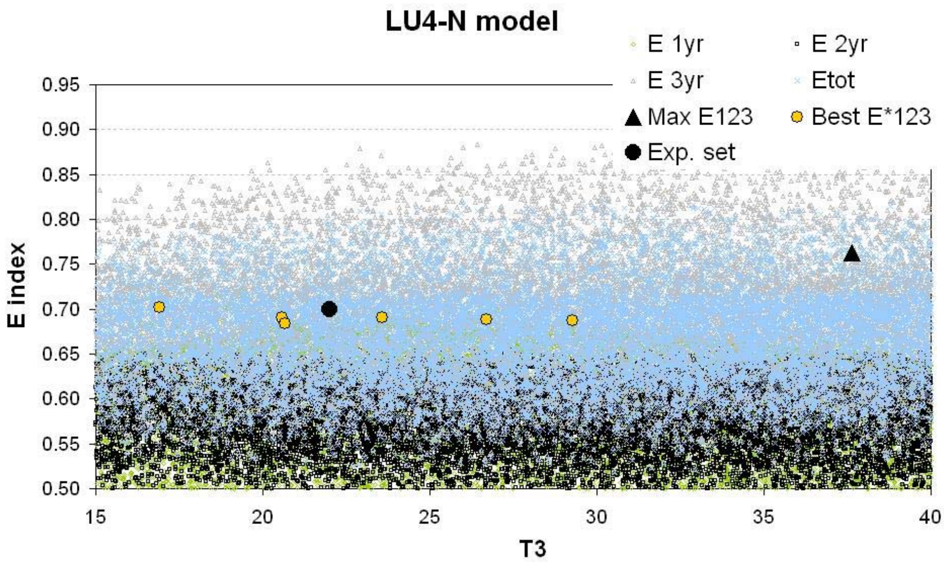


Fig. 3: Continuation; d) T_3 parameter

The best $E_{tot}(Q)$ parameters set and the near-optimum $E^*_{123}(Q)$ parameters sets were tested against additional discharge data observed during a period not included into the calibration one (from August 2002 to June 03). This temporal validation process led to reject the best Monte Carlo parameter sets obtained considering $E_{tot}(Q)$, but to accept those obtained through the multi-objective approach $E^*_{123}(Q)$ (Table 4). Unlike for the hydrological model, for the nitrogen sub-model there are very few simulations that reproduce stream nitrate concentrations acceptably and none that reproduce stream ammonium concentrations data. According to the criteria outlined in section 3, the 100,000 Monte Carlo simulations produced only 21 behavioural parameter sets. To increase the number of behaviours to a level sufficient for the statistical analysis, less severe criteria defining behavioural runs were adopted, such as $RRMSE(NO_3) \leq 0.8$ (instead of 0.6) and $RRMSE(NH_4) \leq 1.4$ (instead of 1.2). With these conditions approximately 1,000 behavioural runs were obtained and Table 3 (column 5) gives the related sensitivity ranking.

Table 4: Different best behavioural parameter sets for the LU4-N model

Hu max	**Ks**	**Kp**	**Kpp**	**T2**	**T3**	**T4**	**Udeep p.**	**Nash validation period**	**BE validation period**	
175.00	25.00	6.00	5.00	2.00	22.00	3000.00	100.00	0.48	28.37	Expert calib.
176.99	36.21	9.63	3.70	1.51	20.58	2888.82	100.56	0.62	43.67	$E^*_{123}(Q)$
167.45	39.80	10.28	12.27	1.51	23.57	3162.89	97.23	0.70	-13.16	$E^*_{123}(Q)$
193.73	29.94	6.47	11.08	1.78	26.70	2316.83	110.72	0.63	3.61	$E^*_{123}(Q)$
199.55	28.87	6.67	11.12	1.67	29.27	2425.92	138.95	0.60	49.45	$E^*_{123}(Q)$
195.30	29.92	8.12	10.96	1.58	20.66	3404.17	122.40	0.68	-4.65	$E^*_{123}(Q)$
165.65	33.92	9.02	9.53	1.90	16.90	2410.13	98.59	0.76	-0.13	$E^*_{123}(Q)$
109.40	39.01	16.24	3.45	1.60	29.62	2315.06	44.92	0.71	49.38	$E_{123}(Q)$
107.29	39.79	13.10	8.44	1.60	28.67	2810.42	58.85	0.18	-43.00	$E_{tot}(Q)$

The results show that streamwater nitrate and ammonium concentrations are especially sensitive to parameters related to the shallow aquifer, in particular the nitrification constant ($K_{nitr-aquif}$), which is in agreement with the conclusion obtained by Medici et al. (2010) regarding the importance of shallow aquifer processes to simulate recession limbs nitrate and ammonium concentrations. Stream nitrate and ammonium concentrations are also sensitive to certain soil parameters, especially the mineralization constant (K_{min}) followed by the annual maximum ammonium uptake ($MaxUP_{NH4}$). These two parameters are directly related with the amount of inorganic nitrogen available to move throughout the soil, hence their importance. The results also clearly highlight that the hydrological model parameters affects inorganic nitrogen simulation; the most influent parameters are H_{u_max} and H_m, which are key factors in determining the amount of water held in soil, thus determining solute concentrations. The thresholds U_{min}, U_{nitr} and U_{immob} determining mineralization, nitrification and immobilisation temporal dynamics were also highlighted as influential.

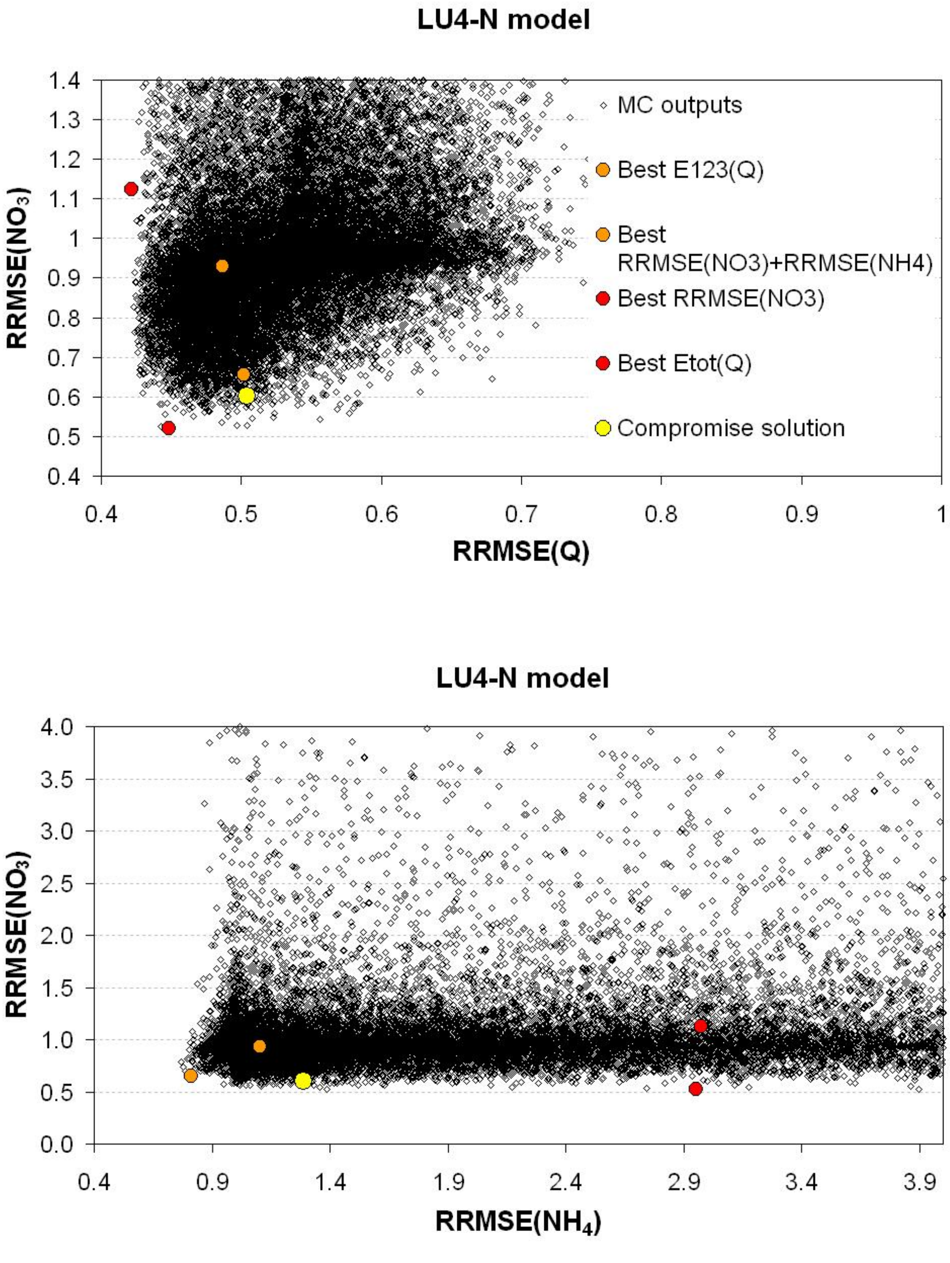
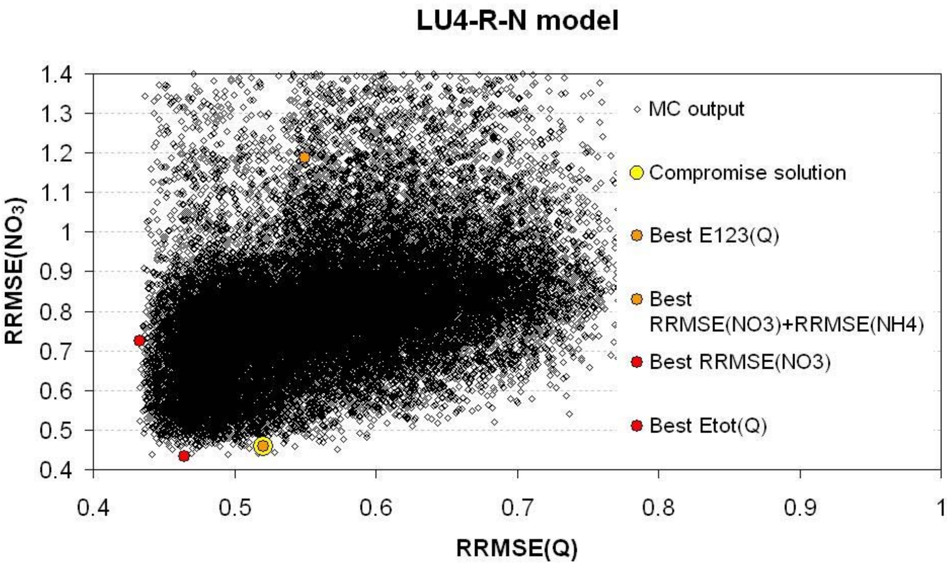


Fig. 4a: Relationships between RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q), illustrating the degree to which the three objective functions were minimized simultaneously with the lumped LU4-N model. The red points represent the best parameter sets corresponding respectively to the smallest value obtained for RRMSE(Q) and RRMSE(NO_3). The two orange points represent parameter sets providing the highest value for E_{123}(Q) and the lowest sum of RRMSE(NO_3) plus RRMSE(NH_4) respectively. The yellow point shows a compromise solution, where an effort is done to take into account simultaneously each annual discharge simulation for nitrate and ammonium.



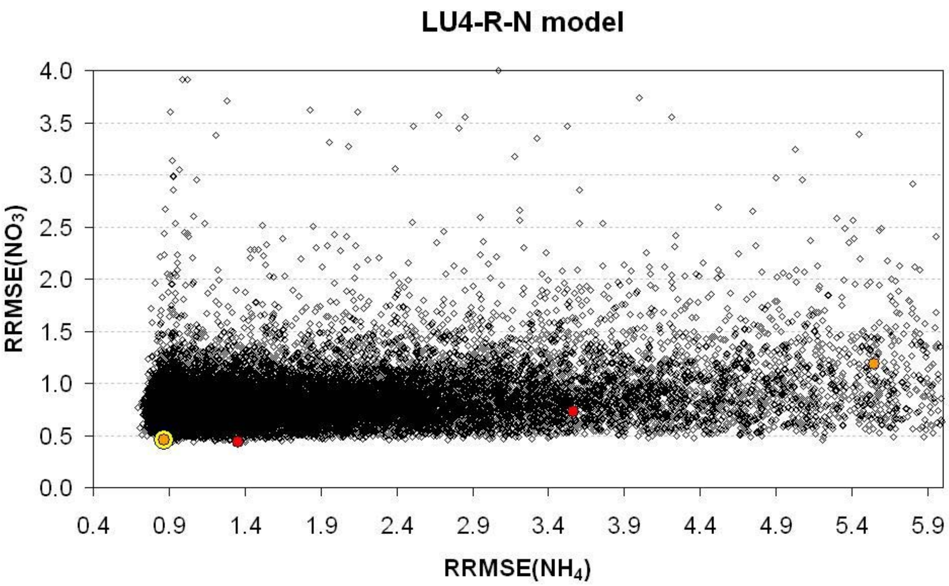
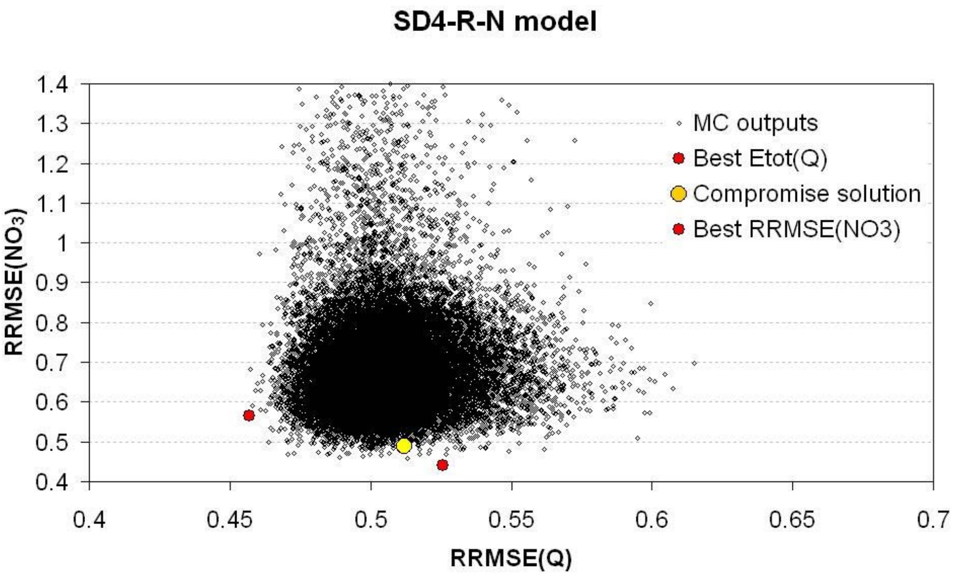


Fig. 4b: Relationships between RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q), illustrating the degree to which the three objective functions were minimized simultaneously with the semidistributed LU4-R-N model.



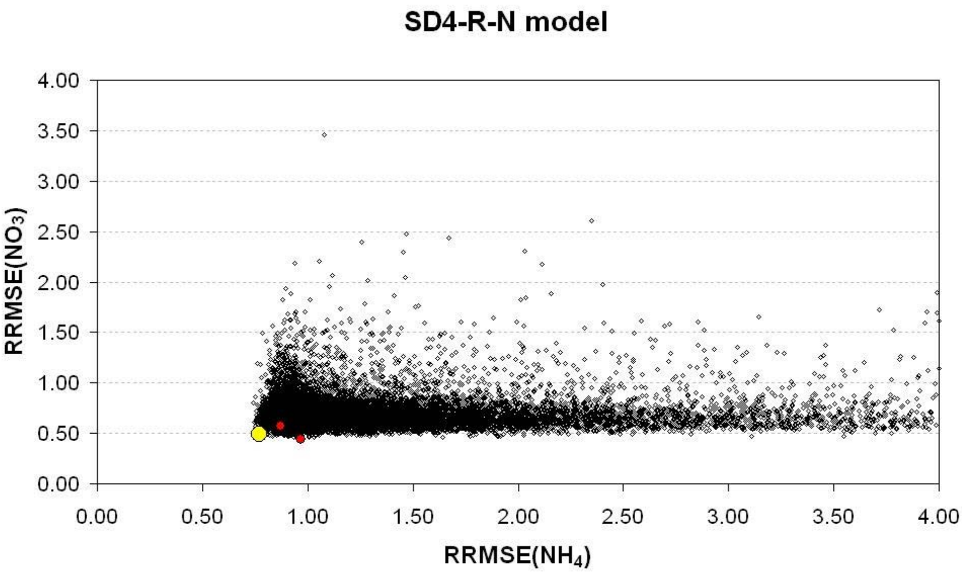
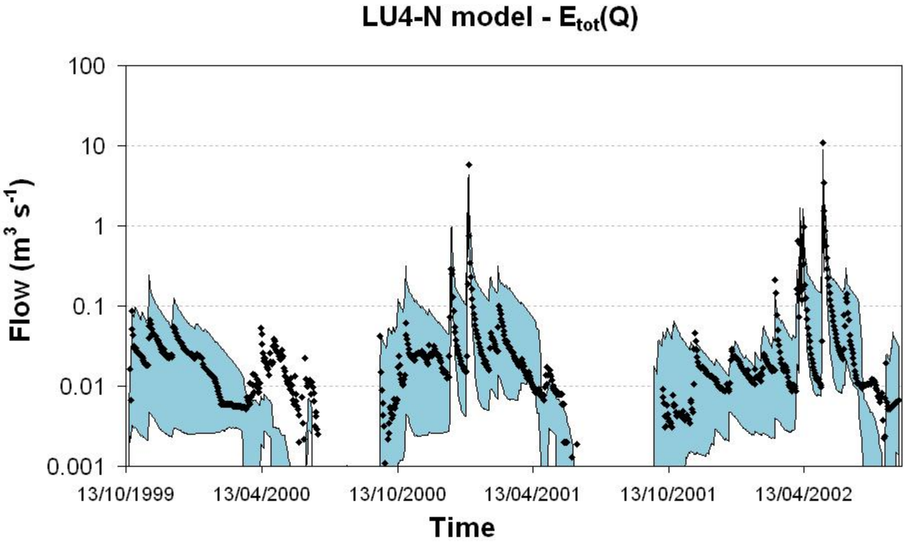


Fig. 4c: Relationships between RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q), illustrating the degree to which the three objective functions were minimized simultaneously with the semidistributed SD4-R-N model.

Figure 4a shows the relationships between RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q_{tot}), illustrating the degree to which the three objective functions were minimized simultaneously. This result shows that the LU4-N model succeeded in achieving near-optimum fits simultaneously to flow and streamwater nitrate, but not ammonium. In this figure the red points represent the best parameter sets corresponding respectively to the smallest value obtained for RRMSE(Q) and RRMSE(NO_3). The two orange points represent parameter sets providing the highest value for E_{123}(Q) and the lowest sum of RRMSE(NO_3) plus RRMSE(NH_4) respectively. It was found that whenever near-optimum parameters sets for nitrogen were taken into account, it generally provided acceptable discharge simulations. On the contrary, the best parameters sets for discharge did not guarantee acceptable nitrate simulations. The N-submodel calibration was repeated varying all the parameters (for flow and nitrogen) at the same time. In this way the RRMSE(NO_3) error, previously obtained fixing the flow parameters at their 'optimum' values prior to calibrating nitrogen processes parameters (Medici et al., 2010), was improved decreasing from 0.54 to 0.48 without getting significantly worse discharge simulation.

a.



b.

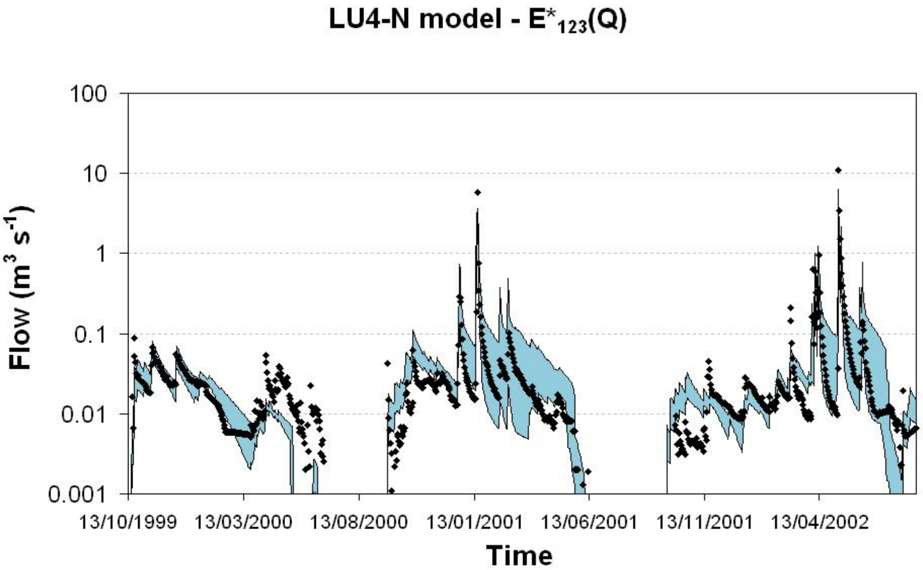


Fig. 5: 1999/2002 observed flow with 5% and 95% GLUE bounds obtained considering a) the $E_{tot}(Q)$ efficiency index and b) the multi-objective approach $E^{*}_{123.}$

Figure 5 shows the observed discharge and the GLUE bounds for the calibration period 1999 to 2002, considering the $E_{tot}(Q)$ efficiency index (Fig. 5a) and the $E^{*}_{123}(Q)$ index (Fig. 5b). The 70.8% of the observed data are included within the 5% and 95% GLUE bounds obtained considering $E_{tot}(Q)$; 16.3% of the observed data are above the upper limit (which means that the model underestimates the observed discharge) and 12.3% are below the lower one (which means that the model over-estimates the observed discharge). Considering the $E^{*}_{123}(Q)$ only 44.7% of the total observed data are included into the calculated GLUE bounds; 18.7% above the upper bound and 36.0% below the lower one. According to the multi-objective approach the LU4-N model clearly underestimates the observed discharge from April to June of the first hydrological year (1999-00) and tends to overestimate the catchment wetting-up. Moreover, the LU4-N model cannot reproduce the highest peaks, though the observed value is illustrative because the storm event was so severe that the field equipment was swept away by the flood (personal observation). Figure 6 shows the observed and predicted bounds for stream nitrate concentration for the calibration period (1999 to 2002). The 59% of the observed stream nitrate concentration are included into the computed GLUE bounds; 29% are above the upper limit and 12% are below the lower one. This shows a model tendency to underestimate nitrate concentration especially after the summer drought and during the catchment drying-up of the first and the third year. The LU4-N model presents a huge spread of values around the highest peak of nitrate concentration observed during March 2002 and it is unable to reproduce the following one observed during April 2002. This result was already highlighted in Medici et al. (2010) as a possible clue that some key mechanism was missing into the LU4-N model conceptual scheme.

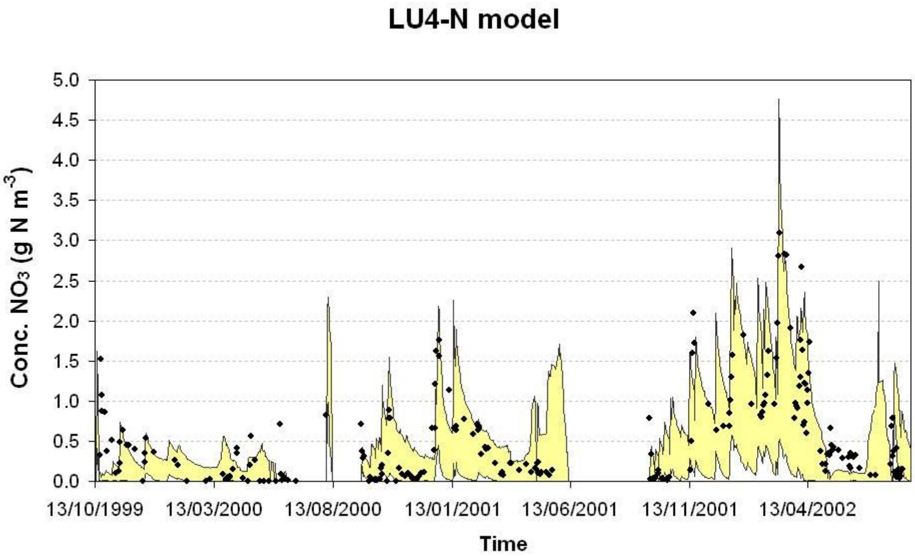


Fig. 6: 1999/2002 observed stream nitrate concentration with 5 and 95% GLUE prediction bounds

4.2 LU4-R-N model sensitivity analysis

This sensitivity analysis of the LU4-R-N model focuses on understanding the influence of the parameters related with the riparian zone, since its inclusion in the model conceptual scheme represents an increase of 13 parameters compared to the LU4-N model. The total number of parameters analysed in this case was 41. The 100,000 Monte Carlo simulations produced 15,784 behavioural outputs considering $E_{tot}(Q)$, 32,298 considering RRMSE(Q) and 8301 considering $E^{*}_{123}(Q)$. In general, the number of behavioural simulations decreased compared to those obtained with the LU4-N model, however the sensitivity ranking obtained is similar to that for the LU4-N model (Table 5, column 2 and 3). The parameters $H_{u\_max\_Hill}$ and H_m still are the most influent ones.

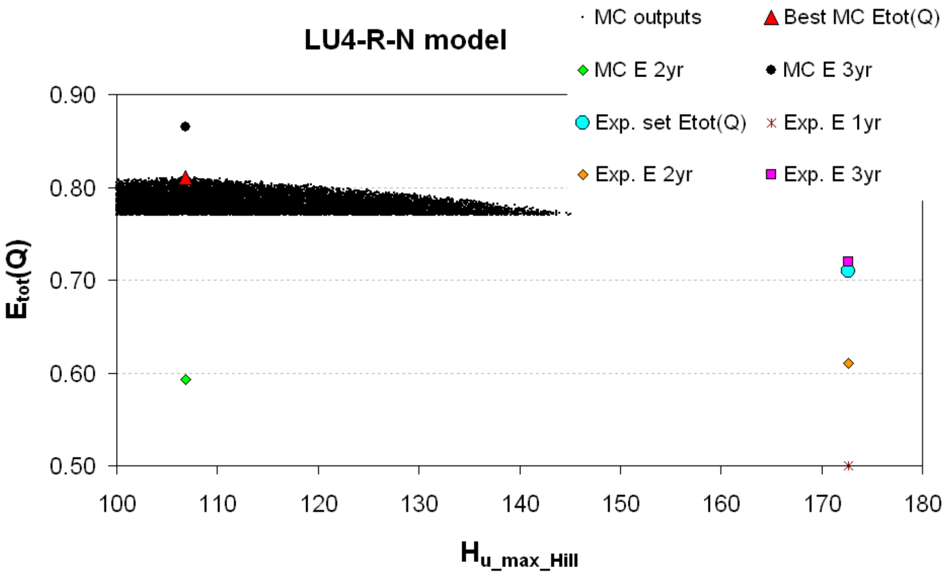


Fig. 7: Scatter plots of the four most flow significant parameters (model LU4-R-N) against the $E_{tot}(Q)$ for the whole calibration period (99-02). The blue circle represents the expert calibration parameter set, while the red triangle represents the best Monte Carlo behavioural parameter set; a) $H_{u\_max\_Hill}$ parameter

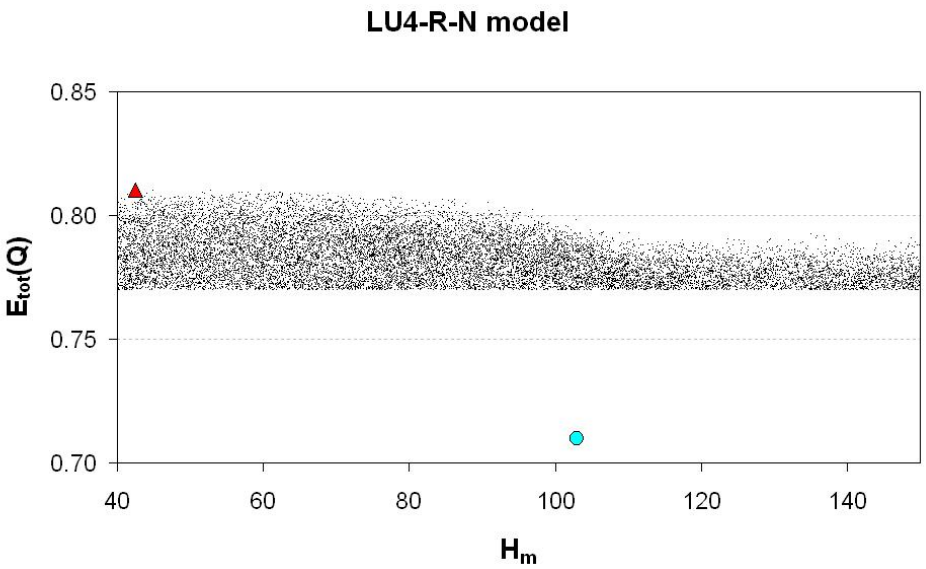


Fig. 7: Continuation; b) H_{max} parameter

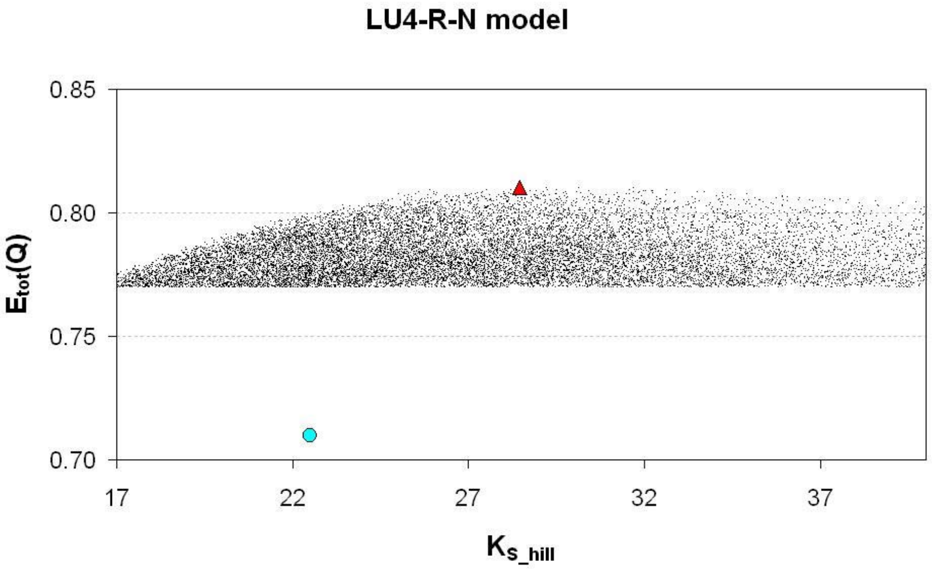


Fig. 7: Continuation; c) K_{s_hill} parameter

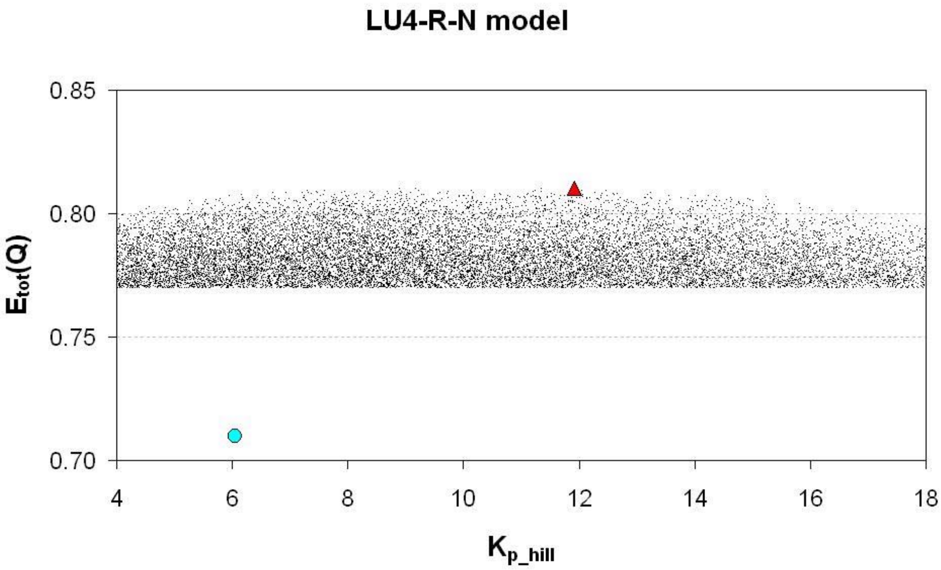


Fig. 7: Continuation; d) K_{p_hill} parameter

The riparian zone related parameters ($H_{u\_max\_ripz}$ and K_{s_ripz}) apparently did not exert any significant influence on the hydrological simulation (Table 5). Despite that, a supplementary analysis was done to test further the actual riparian zone influence on the simulated discharge. In this case, the total number of days (Sim N) during which the simulated discharge can be considered negligible (simulated Q less than 0.001 m^3s^{-1}, see Medici et al., 2008) was introduced as an additional behavioural criteria to take into account model ability to reproduce the summer drought. Explicitly, the thresholds of acceptability were set at Sim N ≥ 200 days and Sim N ≤ 280 days, being 220 the observed total number of days during which the stream can be considered dry. Once the specific conditions about the length of the dry period were included, the parameter sensitivity ranking highlighted $H_{u\_max\_ripz}$ as influential on discharge simulation. Thus, for the rainfall-runoff modelling of the Fuirosos catchment, the riparian zone seems to exert its influence over a very specific hydrograph characteristic that is the catchment drying-up and wetting-up, supporting the conclusion pointed out in Medici et al. (2008).

Figure 8 shows the scatter plot of the LU4-R-N most sensitive parameter ($H_{u\_max\_Hill}$) against each annual E index as well as $E_{tot}(Q)$. The behaviour outlined is similar to the one obtained with the LU4-N model. The triangle represents the parameter set that leads to the highest value of $E_{123}(Q)$, while the yellow points represent near-optimum parameter sets for $E^*_{123}(Q)$. The best parameters space for $E^*_{123}(Q)$ includes the expert parameter set, suggesting again that the $E^*_{123}(Q)$ multi-objective approach is the most suitable to represent the high inter and intra-annual hydrological variability of this Mediterranean catchment.

Considering the nitrogen sub-model, the 100,000 Monte Carlo simulations produced 1534 behavioural outputs, which represent a significant increment compared with the initial 21 behavioural parameters sets obtained with the LU4-N model. Table 5 (column 5) gives the sensitivity ranking obtained. The most influential parameter for nitrogen simulation is

$H_{u\_max\_Hill}$, which is closely followed by the hillslope mineralization constant (K_{min_Hill}). In fact, it can be said that this two parameters predominantly control the amount of water and inorganic nitrogen (as ammonium) available to be routed and transformed throughout the catchment. Riparian local aquifer nitrification/denitrification processes ($K_{nitr\_aq\_ripz}$ and $K_{denitr\_aq\_ripz}$) were stressed also as influential for the inorganic nitrogen simulation. On the contrary, parameters related to the biological processes in the riparian zone soil seem to be non influential on the nitrogen simulation; however it has to be taken into account that the riparian zone represents a very small portion of the catchment area (approximately 0.5% of the total catchment area).

The results give also a clear indication of the key role played by the hillslope perched water table in terms of both inorganic nitrogen behaviour ($K_{denitr\_aquif\_hill}$ and $K_{nitr\_aquif\_hill}$) and discharge (e.g.: T_3, H_m and K_{pp}).

Table 5: Sensitivity ranking of LU4-R-N model parameters based on KS statistic

	LU4-R-N model			
Parameter name	**RRMSE(Q)≤0.5**	**E_{tot}(Q)≥0.77**	**E^{*}_{123}(Q)≥1.5**	**RRMSE(NO3)≤0.6 RRMSE(NH4)≤1.2**
Hu max hill	1 (0.744)	1 (0.736)	1 (0.497)	1 (0.365)
Ks hill	3 (0.219)	3 (0.187)	4 (0.209)	
Kp	4 (0.149)	4 (0.140)	3 (0.299)	13 (0.071)
Kpp	6 (0.069)	6 (0.050)	6 (0.056)	15 (0.059)
T2	5 (0.146)	5 (0.129)	5 (0.162)	17 (0.056)
T3	7 (0.041)	7 (0.049)	7 (0.037)	
T4				
H_m	2 (0.407)	2 (0.324)	2 (0.419)	6 (0.180)
Hu max ripz				20 (0.044)
Ks ripz				
Kmin hill.				2 (0.323)
Knitr hill.				
Kimm hill.				18 (0.051)
Kdenitr hill.				
Kdenitr_aquif hill.				7 (0.157)
Knitr_aquif hill.				4 (0.216)
Kmin ripz				
Knitr ripz				
Kimm ripz				
Kdenitr ripz				
Kdenitr_aquif ripz				5 (0.196)
Knitr_aquif ripz				12 (0.079)
Kads				11 (0.087)
Kdes				19 (0.049)
$KupNH_4$				21 (0.042)
$KupNO_3$				
$KupNH_4$ ripz.				
$KupNO_3$ ripz.				
Udenitr hill.				
Uimm hill.				8 (0.127)
Umin hill.				9 (0.119)
Unitr hill.				10 (0.088)
Udenitr ripz				16 (0.057)
Uimmob ripz				
Umin ripz.				
Unitr ripz.				
$MaxAdsNH_4$				14 (0.070)
$MaxUPNH_4$				3 (0.317)
$MaxUPNO_3$				
$WMaxUPNO_3$				
C_9				

Figure 4b shows the relationships between RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q_{tot}), illustrating the degree to which the three objectives have been minimized simultaneously. The LU4-R-N model succeeded in achieving near-optimum fits simultaneously to flow and nitrate, but not ammonium. As for the LU4-N model, the best parameters sets for the discharge, most of time, did not provide acceptable inorganic nitrogen simulations, while the best parameters sets for nitrogen often underlined feasible discharge simulations.

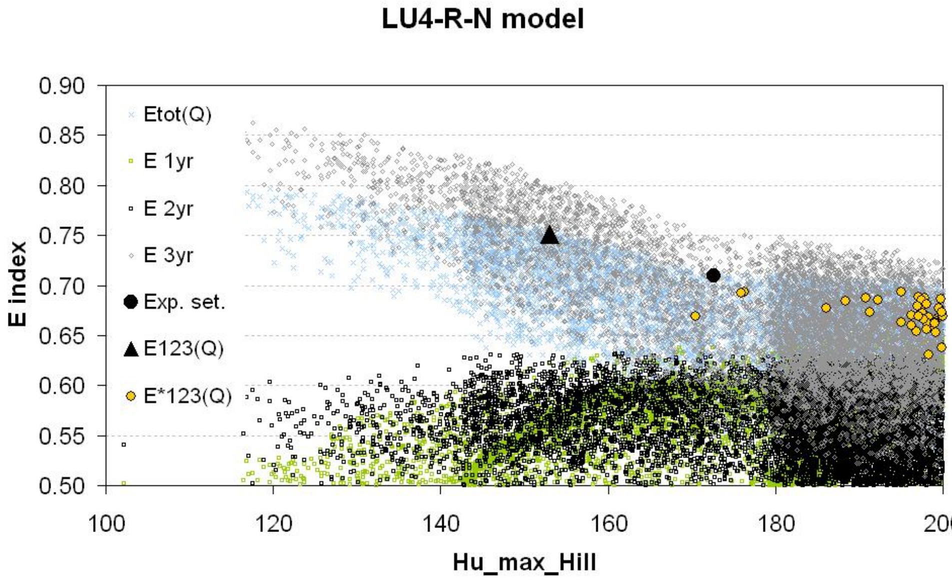
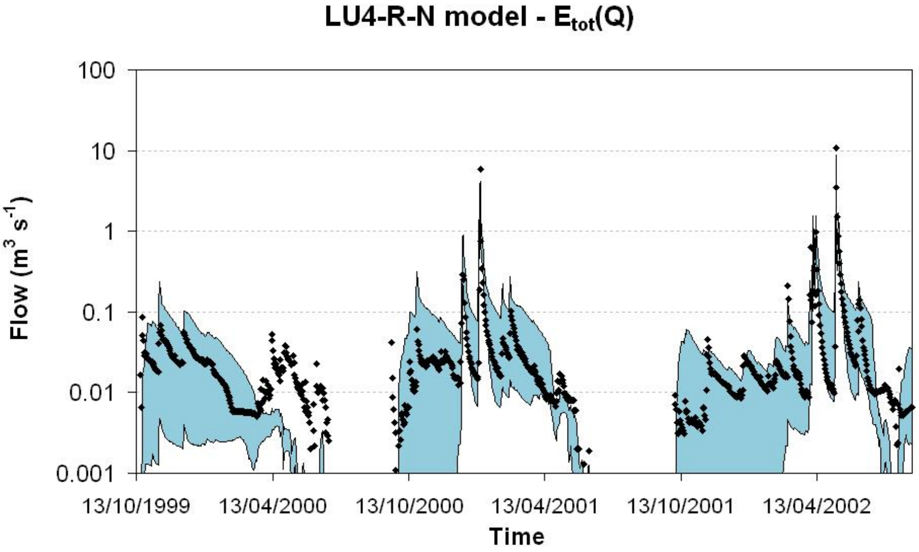


Fig. 8: Scatter plots of the most influential parameter (model LU4-R-N) considering the multi-objective approach E^*_{123}. The black point representing the expert calibration; the triangle representing the best E_{123} behavioural parameter set and finally the yellow rhombus representing the near optimum parameters sets according to the multi-objective approach E^*_{123}.

Figure 10 shows the GLUE discharge bounds for the calibration period 1999-02 considering both $E_{tot}(Q)$ efficiency index (Fig. 9a) and the multi-objective $E^*_{123}(Q)$ index (Fig. 9b). In the first case, the 76% of the observed data are included into the calculated GLUE bounds; 21% are over the upper limit, while 3% are under the lower one. In the second case (Fig. 9b), 58% of the observed discharges are included into the obtained GLUE band; 22% are above the upper limit and 20% are below the lower one. The LU4-R-N model clearly underestimates the discharge from April to June of the first hydrological year (1999-00) and the highest discharge peaks, as in the case of the LU4-N model. Interestingly, considering $E_{tot}(Q)$, the spread of the simulated values around the observed discharge during the catchment wetting-up increased significantly (Fig. 9a) compared with that of the LU4-N model, which seems to be directly linked with the riparian zone introduction into the catchment conceptual model.

a.



b.

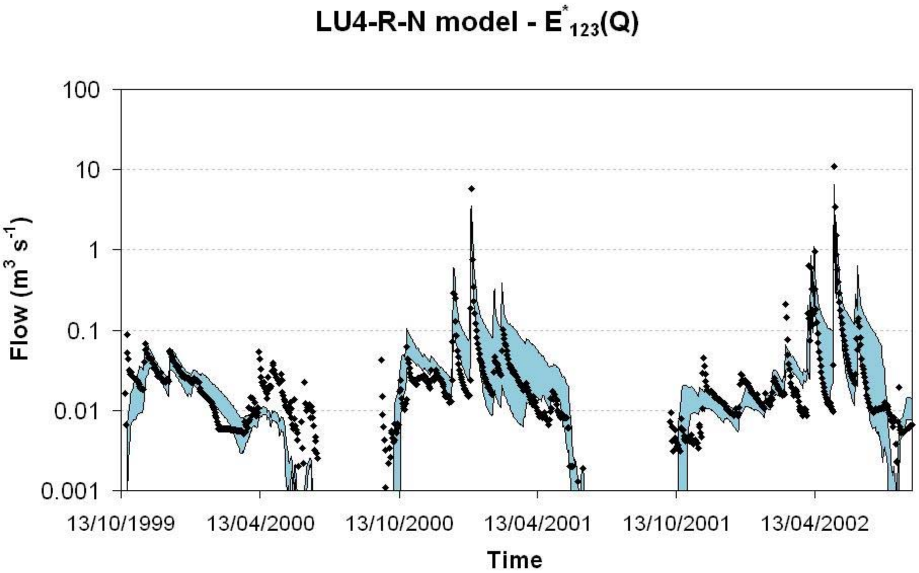


Fig. 9: 1999/2002 observed flow with 5 and 95% GLUE bounds obtained considering a) the $E_{tot}(Q)$ efficiency index and b) the multi-objective approach E^*_{123}

Once the multi-objective approach $E^*_{123}(Q)$ is taken into account (Fig. 9b) the GLUE bound are similar to those obtained for the LU4-N model (Fig. 5b), though the percentage of observed data included is higher. The 5% and 95% GLUE band for stream nitrate concentration (Fig. 10) is wider than that for the LU4-N model, thus it includes 68.3% of the observed data; 15.5% of the observed data are above the upper limit, while 16.3% are below the lower one. To point out that the width of the GLUE bound around the highest stream observed nitrate concentration slightly decreased compared to that of the LU4-N model and it also includes the second highest nitrate concentration observed during May 2002. Medici et al (2010) previously linked LU4-R-N model's ability in reproducing both these two nitrate peaks with the role played by the riparian zone.

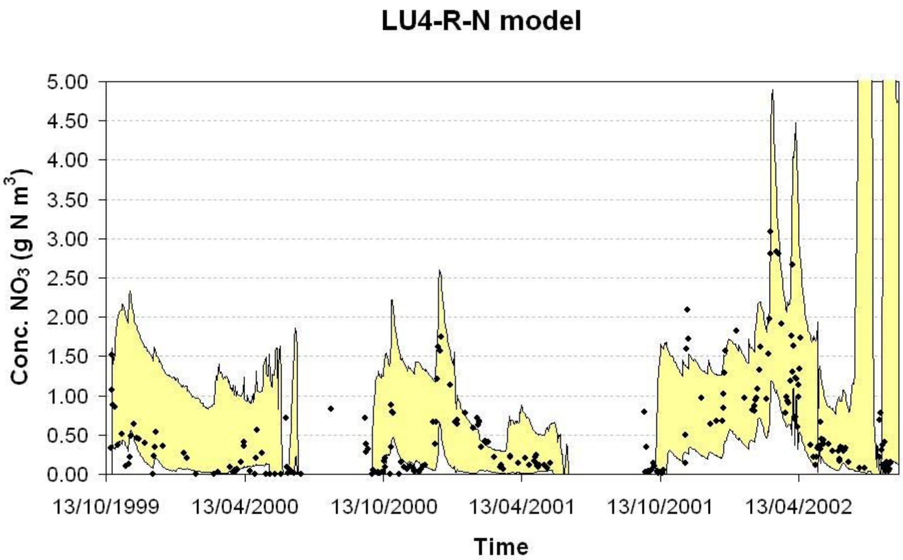


Fig. 10: 1999/2002 observed stream nitrate concentration with 5 and 95% GLUE bounds.

4.3 SD4-R-N model sensitivity analysis

The sensitivity analysis of the SD4-R-N model focuses on understanding the influence of more distributed spatial representation of rainfall-runoff model parameters.

The total number of parameters analysed in this case was 59, 28 for the hydrological model and 31 for the N model as for the LU4-R-N model. 100,000 Monte Carlo simulations produced only 2,805 behavioural outputs considering $E_{tot}(Q)$, around 5,034 considering RRMSE(Q) and 3,084 considering $E^{*}_{123}(Q)$.

Table 6 gives the sensitivity ranking; it shows that almost all the hydrological model parameters for each HRU (leucogranite, granodiorite and sericitic schists) exert some influence on the global objective functions $E_{tot}(Q)$ and RRMSE(Q), as well as on the multi-objective function $E^{*}_{123}(Q)$. Not surprisingly the first places of the sensitivity ranking are occupied by the parameters related with the leucogranit lithological unit, which is the largest among the three main lithological units. In particular, $H_{u\_max\_leuco}$ and H_{m_leuco} are by far the most influential parameters. This is in the same line of the results previously obtained with LU4-N and LU4R-N models and once again the importance of introducing a soil moisture threshold to simulate non-linear deep percolation was highlighted. An additional analysis considered the Grimola sub-catchment discharge (Medici et al., 2008) that is a tributary of the Fuirosos stream, draining approximately 4 km^2 (Fig. 1). The same procedure based on the evaluation of the KS statistic was repeated considering only the Grimola sub-catchment simulation, obtaining an equal sensitivity ranking as the one obtained for the Fuirosos catchment. Hence, it suggests that the sensitivity ranking is uniform down the river. Even if, comparing Grimola and Fuirosos flow near-optimum parameter values (Fig. 11), it was shown that for the former, H_{u_max} tends to have generally higher values, which may suggest that a specific parameterization for the catchment headwater, concerning in particular this influent parameter, could improve model simulations.

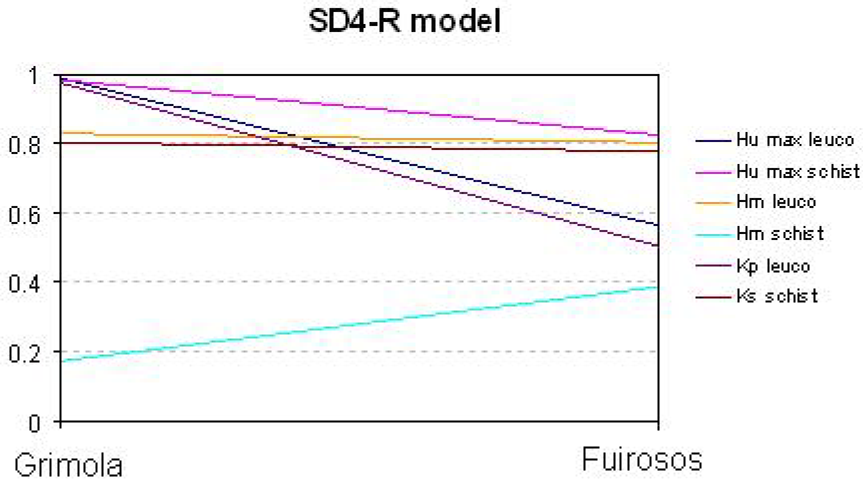


Fig. 11: Variation of flow-optimum parameter values down the river (form Grimola to Fuirosos outlet point). The parameters values (y-axis) are rescaled using the prior bound as 0 and 1.

Table 6: Sensitivity ranking of SD4-R-N model parameters based on KS statistic

	SD4-R-N model			
Parameter name	**RRMSE(Q)≤0.5**	**E_{tot}(Q)≥0.77**	**E^{*}_{123}(Q)≥1.5**	**RRMSE(NO3)≤0.6 RRMSE(NH4)≤1.2**
Hu max leuco.	1 (0.514)	1 (0.547)	1 (0.538)	15 (0.058)
Hu max grano.	6 (0.189)	6 (0.230)	10 (0.117)	12 (0.064)
Hu max schst.	12 (0.084)	12 (0.105)	2 (0.338)	7 (0.080)
Hu max ripz.				18 (0.043)
Ks leuco.	4 (0.234)	4 (0.273)	3 (0.241)	
Ks grano.	15 (0.055)	16 (0.062)	18 (0.029)	
Ks schst.	3 (0.262)	3 (0.295)	9 (0.118)	20 (0.039)
Ks ripz.		19 (0.029)		
Kp leuco.	7 (0.175)	7 (0.204)	8 (0.118)	
Kp grano.	19 (0.025)		15 (0.038)	23 (0.037)
Kp schst.	14 (0.067)	15 (0.071)	11 (0.108)	
Kpp grano.	16 (0.054)	17 (0.056)		
Kpp leuco.	5 (0.202)	5 (0.231)	7 (0.125)	
Kpp sch.	10 (0.097)	10 (0.116)	13 (0.075)	19 (0.043)
T2 grano.	13 (0.081)	13 (0.102)	14 (0.059)	28 (0.028)
T2 leuco.	11 (0.086)	8 (0.122)	5 (0.148)	
T2 schst.	15 (0.066)	14 (0.079)	16 (0.034)	13 (0.061)
T3 grano.				
T3 leuco.	18 (0.039)	18 (0.046)		24 (0.032)
T3 schst.			17 (0.030)	
T4 schst.				29 (0.029)
H_m grano.	9 (0.102)	11 (0.114)	12 (0.093)	
H_m leuco.	2 (0.404)	2 (0.432)	6 (0.130)	
H_m schst.	8 (0.114)	9 (0.121)	4 (0.193)	10 (0.068)
Kmin hill.				1 (0.526)
Knitr hill.				
Kimm hill.				14 (0.059)
Kdenitr hill.				
Kdenitr_aquif hill.				6 (0.083)
Knitr_aquif hill.				4 (0.108)
Kmin ripz				16 (0.015)
Knitr ripz				
Kimm ripz				
Kdenitr ripz				
Kdenitr_aquif ripz				2 (0.248)
Knitr_aquif rip				9 (0.069)
Kads				21 (0.039)
Kdes				26 (0.029)
$KupNH_4$				17 (0.051)
$KupNO_3$				27 (0.028)
$KupNH_4$ ripz.				
$KupNO_3$ ripz.				

Udenitr hill.	5 (0.099)
Uimm hill.	
Umin hill.	25 (0.031)
Unitr hill.	
Udenitr ripz	22 (0.038)
Uimmob ripz	3 (0.198)
Umin ripz.	8 (0.076)
Unitr ripz.	11 (0.063)
$MaxAdsNH_4$	
$MaxUPNH_4$	
$MaxUPNO_3$	
$WMaxUPNO_3$	
C_9	

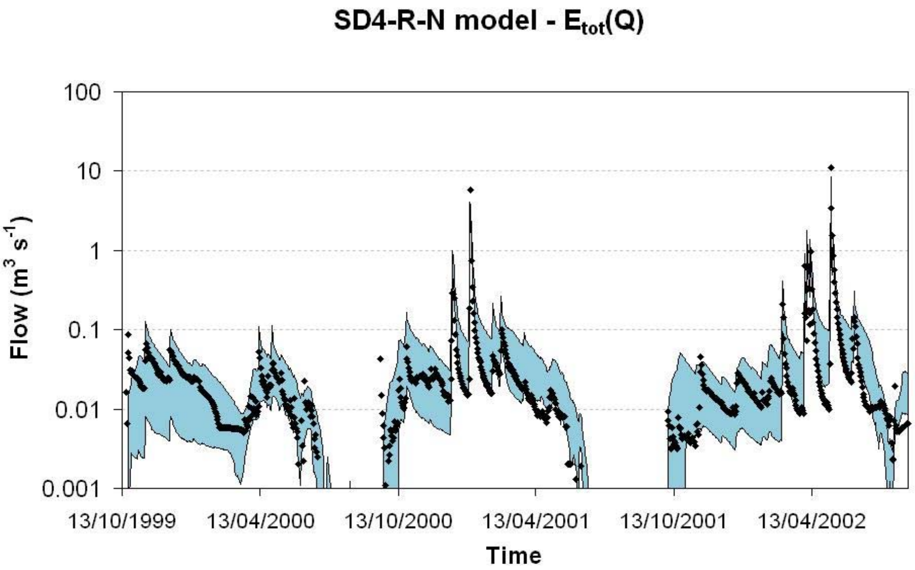
The objective functions E_{tot}(Q) and RRMSE(Q) do not seem to be sensitive to the riparian zone parameters, as was found for the LU4-R-N model. However, when specific indexes for the summer drought period were taken into account, the riparian zone parameters gained importance.

Concerning the nitrogen sub-model, 100,000 Monte Carlo simulations produced approximately 3,000 behavioural outputs, which represent a considerable increment compared with the number obtained with the LU4-N model and also LU4-R-N model. Table 6 gives (column 5) the obtained sensitivity ranking. The most influential parameter is the hillslope mineralization constant (K_{min_Hill}), followed by the riparian local aquifer denitrification constant ($K_{denitr\_aquif\_ripz}$) and the riparian zone immobilization threshold (U_{immob_ripz}). Moreover, all the soil moisture thresholds that govern riparian zone biological process exert certain influence in the inorganic nitrogen dynamic.

Also for the SD4R-N model, the sensitivity analysis highlighted the hillslope perched water table related parameters as quite influential (e.g. $K_{denitr\_aquif\_Hill}$, $K_{nitr\_aquif\_Hill}$ and also H_{m_schst}, Table 6: column 5).

Scatter plots of RRMSE(NO_3), RRMSE(NH_4) and RRMSE(Q) versus each other (Fig. 4c) showed that a near-optimal solution could be found simultaneously for flow and nitrate. The model also improved its ability to reproduce stream ammonium concentrations, as can be seen in figure 4c (right panel). As for the LU4-N and LU4-R-N models, also for the SD4R-N model the parameters sets leading to near-optimum solutions for nitrate generally provided satisfactory discharge simulations, only slightly worse than that obtained with discharge near-optimum parameters sets. Hence, a simultaneous calibration of all the most model sensitive parameters led to improve inorganic nitrogen simulation without getting notably worse discharge simulations.

a.



b.

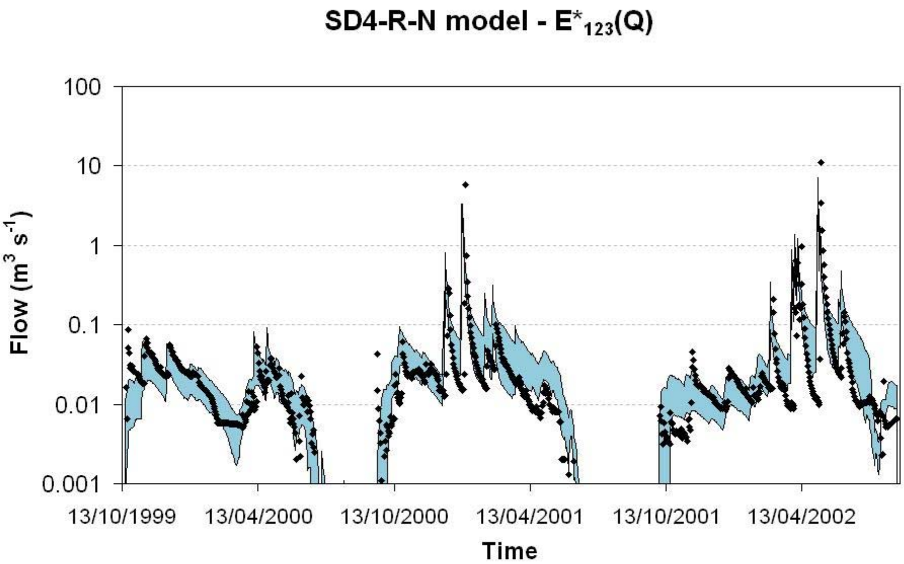


Fig. 12: 1999/2002 observed flow with 5 and 95% GLUE prediction bounds obtained considering a) the Etot(Q) efficiency index and b) the multi-objective approach $E^*_{123.}$

Figure 14 shows the observed discharge and GLUE bounds for the calibration period from October 1999 to August 2002, considering both the $E_{tot}(Q)$ efficiency index (Fig. 12a) and the $E^{*}_{123}(Q)$ index (Fig. 12b). Despite the increased number of parameters, the GLUE band obtained for the SD4-R-N model is narrower than that for the LU4-R-N model, though it includes almost the same percentage of observed data: 75% of the total observed data; 6% are over the upper limit, while 19% are below the lower one. Considering the multi-objective approach $E^{*}_{123}(Q)$, 64% of the observed data are within the GLUE band (Fig. 12b) that in terms of average width is equivalent to that of the LU4-N and LU4-R-N model but it includes a higher percentage of observed data; 7% of the observed data are over the upper limit and 29% are below the lower one. Overall, the results stress that the SD4-R-N model is able to reproduce satisfactorily the three hydrological years simultaneously. However, it presents a slight tendency to overestimate the recession curves, especially during the wet period. Finally, Figure 13 shows the observed and GLUE bounds for stream nitrate concentration, which includes 61% of the observed data; 24% of the observed concentrations are over the upper limit, while 16% are below the lower one. The total number of observed data included into the SD4-R-N GLUE band is lower than in the case of the LU4-R-N, but the spread of the simulated values around the observed ones is significantly smaller. Moreover, the SD4-R-N is able to reduce the error associated to the highest nitrate concentration peaks observed during the third year (2001-02).

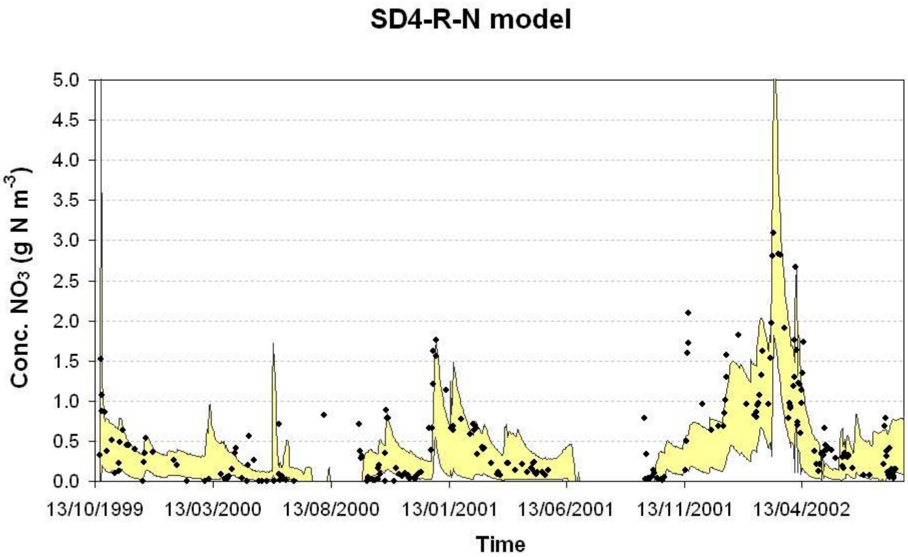


Fig. 13: 1999/2002 observed stream nitrate concentration with 5 and 95% GLUE prediction bounds

5. Discussion

The analysis presented in this paper pointed out some interesting results and allows answering the questions set at the beginning. Concerning discharge simulation, in all the cases the parameter H_m was always among the most influential parameters. This parameter controls when percolation to the permanently saturated zone may occur (which is during wet conditions or during extreme rainfall events) and the formation of a perched shallow aquifer (when the surface redistribution of rainfall is more difficult). In fact, in Mediterranean and semi-arid systems water flowpaths are essentially different during wet and dry conditions (Gallart et al., 2002) and the formation of a perched shallow aquifer was highlighted as an important mechanism (Ocampo, 2006). In addition, the hydrological parameters that define the amount of water generating the interflow (K_s) and the two different base flows (K_p and K_{pp}) were pointed out in all the cases as influential in simulating the hydrological catchment response. Consequently this result supports the four hydrological responses conceptual scheme adopted.

The non-linear inorganic nitrogen behaviour led to include into the model scheme also other threshold mechanisms (U_{min}, U_{nitr}, U_{imm} and U_{denitr}) in order to simulate soil processes 'pulse' behaviour, previously observed in several Mediterranean and semi-arid environments (Birch 1959, 1960, and 1964; Mummey et al., 1994, Schiwinning et al. 2004 and 2004). The sensitivity analysis, generally pointed out that thresholds as influential on nitrogen simulation.

Another mechanism that was taken into account to improve the representation of this small Mediterranean forested catchment was the riparian zone. This implied an enlarged number of parameters to be calibrated (section 4.2). The riparian zone parameters were not significantly influential on discharge simulation, unless taking into account the total number of days during which the simulated discharge can be considered negligible. This also highlights the importance of choosing adequate objective functions for the sensitivity analysis to avoid getting wrong conclusions about the influence exerted by certain parameters or mechanisms in order to simplify models structures. Also, it points out that is particularly important choosing a significant period for the calibration process that might include a wide range of conditions where different catchment processes are activated (Gupta and Sorooshian, 1985; Yapo et al., 1996, after Wagener et al. 2004).

For stream nitrate and ammonium concentration several riparian zone parameters (Table 5 and 6) were pointed out as influential, but overall the ones related with the nitrification and denitrification processes occurring in the local riparian aquifer. This result is interesting since several authors have already stressed the stream-riparian zone system as quite active area in terms of nitrogen cycle (Butturini et al., 2002 and 2003, Von Schiller et al., 2008).

The parameters sensitivity ranking slightly changes when considering a single objective function approach - $E_{tot}(Q)$ or RRMSE(Q) - or a multi-objective approach as $E^{*}_{123}(Q)$. In this case, the use of only an objective function gave more importance to those parameters directly related with the production of the discharge peaks, which generally meant poor results concerning low flow simulation. On the contrary, when the multi-objective approach was taken into account, parameters related with the low flow dynamic gained importance. This is because the model is forced to simulate adequately each hydrological year, particularly the first one during which the base flow dominates. Moreover adopting a multi-objective approach, the near-optimum Monte Carlo parameters sets obtained for discharge were usually close to the expert calibrated one, achieved through a systematic manual process (Medici et al., 2008). In the case of Mediterranean catchments the multi-objective approach is thought to be particularly important to simulate adequately their hydrological response given their characteristic high inter and intra-annual variability. This approach helped to address the identifiably parameters problem, as also found by Gupta et al. (1998), who demonstrated that models can be better constrained using multi-objective approach based on a range of statistics to describe the agreement between predicted and observed stream flow. As a matter of fact, the number of behavioural simulations decreased when the multi-objective approach was considered since the parameters sets had to fulfil more demanding criteria. This fact is also reflected by the comparison between the GLUE bounds (Figs. 5, 10 and 14) obtained from behavioural parameters sets defined by a single objective function (wider GLUE band) and that defined by a multi-objective function (narrower GLUE band).

The sensitivity analysis clearly pointed out the influence of rainfall-runoff parameters on the inorganic nitrogen simulation, hence stream nitrate and ammonium concentrations may also help to constrain rainfall-runoff parameters values and to discard some hydrological mechanisms in favour of others. In fact, considering simultaneously all the behavioural criteria outlined in section 4, for discharge and inorganic nitrogen, the number of behavioural outputs dramatically decreased: none with the LU4-N model, 59 with the LU4-R-N model and 127 with the SD4-R-N model.

Another important result is that, for the discharge, the number of behavioural runs decreased with model complexity, but model's ability to simulate the observed streamflow increased. In fact, the portion of observed data included into the GLUE band, considering the multi-objective approach (Fig. 5b, 10b and 14b), increased from 45% with the LU4-N to 63% with the SD4-R-N. The reduced number of behavioural outputs as model's complexity increases suggests less models degrees of freedom, which can be explained taking into account the progressive introduction of additional catchment estimated characteristics, such as the four small reservoirs (Section 2, Fig. 1) and evapotranspiration spatial variability according to HRUs main representative aspect and vegetation (Medici et al., 2008). These additional features seem to help the conceptualization to gain consistency and so to constrain parameters values and reduce the number of possible parameters combinations leading to behavioural outputs.

On the contrary, considering nitrate, the number of behavioural runs increased with model's complexity from 21 with the LU4-N model to approximately 3,000 with the SD4-R-N model. The inclusion of the riparian zone seems to be the main responsible for the enhanced LU4-R-N and SD4-R-N models ability to simulate stream nitrate concentration. On one hand, in the case of the LU4-R-N the riparian zone led to get wide GLUE bands, in particular for stream nitrate concentrations, which can be explained considering the larger number of parameters to be calibrated and the increased model's degrees of freedom. On the other hand, the SD4-R-N model presents narrower GLUE bounds than the LU4-R-N model, which points to increased model robustness. This is an interesting result taking into account the larger number of parameters of the SD4-R-N model. However, it has to be kept in mind that the SD4-R-N and LU4-R-N models have exactly the same nitrogen conceptual scheme (same N-parameters) and that the increment of parameters is related just to the rainfall-runoff scheme. Therefore, it seems that the more detailed semi-distributed description of the soil characteristics and evapotranspiration led to an improvement in discharge simulation that also improved model's ability to reproduce the observed stream nitrate concentrations. So, the larger number of nitrate behavioural outputs could be related with SD4-R-N reliability in representing how the Fuirosos catchment works. To this end, Dean et al. (2009) states that it is well known that any water quality model can only be as good as the water quantity model driving.

6. Conclusion

In this work an extensive regionalised sensitivity analysis based on Monte Carlo simulations was done to three nitrogen models of increasing complexity in application to the Fuirosos catchment, Catalonia. The main results obtained are: 1) the thresholds mechanisms introduced to simulate the non linear hydrological and nitrogen Fuirosos catchment behaviour were pointed out in all cases as influential on model results; 2) Riparian local aquifer nitrification/denitrification processes ($K_{nitr\_aq\_ripz}$ and $K_{denitr\_aq\_ripz}$) were stressed as influential for the inorganic nitrogen simulation, which support the idea that stream-riparian zone system represents an important mechanism to take into account to simulate inorganic nitrogen; 3) Multi-objective approaches are particularly important for suitably calibrated Mediterranean and semi-arid systems due to their characteristic high inter and intra-annual variability and helped to constrain parameter values; 4) The number of behavioural outputs for stream-water discharge decreases with model complexity, but the portion of observed data included within the 5% and 95% GLUE bounds gets larger (Fig. 5b, 10b and 14b), suggesting an increasing models ability in simulating properly the observed data; 5) The number of behavioural outputs for nitrate increases with model complexity, which in the case of the LU4-R-N model has been explained considering the higher degrees of freedom due to the introduction of the riparian zone, while in the case of the SD4-R-N model seems to be more related with the improvement in reproducing the observed discharge. As a matter of fact, the SD4-R-N model present narrower GLUE bounds than the LU4-R-N model (despite the increase number of rainfall-runoff parameters to be calibrated), but it includes almost the same percentage of observed streamwater nitrate concentrations data; 6) Catchment inorganic nitrogen dynamic is definitely influenced by hydrological models parameters and it was shown that generally nitrogen near-optimum parameters sets underlie acceptable discharge parameters sets. This led to a simultaneous calibration of all the most sensitive models parameters, which was revealed as the best calibration strategy and finally 7) the number of equally good parameters sets decreased enormously when hydrological and water quality are modelled simultaneously. Hence, water quality modelling seems to be less affected by the equifinality problem (as it was defined by Beven, 2001), than just rainfall-runoff modelling.

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5

Conclusions

The important thing is not to stop questioning.
Curiosity has its own reason for existing.

Albert Einstein

5.1 Concluding remarks

The hydrological and water quality modelling of semi-arid regions such as those in the Mediterranean is a complex challenge and an unresolved problem that could be better addressed by an appropriate hydrological and biogeochemical conceptualization of these systems. The present study is an attempt to identify the key processes governing the hydrological and inorganic nitrogen cycle of a small Mediterranean forested catchment (Fuirosos) by means of progressive perceptual modelling (following Piñol et al., 1997) with the ultimate aim of extrapolating the findings to other Mediterranean catchments. To this end, Beven (2009) stated that setting the modelling problem in the context of a learning framework for specific places allows a gradual refinement of how places are represented. In this work, catchment modelling was used as a deductive tool to explore the performance of a system of interest as if it had the features corresponding to a certain set of assumptions. Certainly, it is not possible to claim that if the hydrology and/or streamwater nitrate concentrations are successfully simulated by the model, then this provides an inference that the process caused the observed response. However, soft data regarding the hydrological and inorganic nitrogen behaviour of the catchment were exploited where possible and qualitative knowledge was used to achieve a more realistic description of the catchment behaviour.

The hydrological modelling of the Fuirosos catchment led to a perceptual model that involves four different hydrological flow-paths: a) overland flow, associated with water flowing over the surface or in the organic horizon (horizon O); b) interflow that occurs in the soil-gravel layer (horizon A); c) quick base flow represents the flow that occurs into the upper part of the weathered bedrock (horizon B); and d) slow base flow associated with the permanently saturated zone within the deeper weathered bedrock layer (deep aquifer).

Three recognizable periods within the same hydrological year can be identified in Fuirosos, as for other Mediterranean systems (Piñol et al., 1997; Gallart et al., 2002; Latron 2003): a long dry season; a wetting-up period (during which large rainfall events may produce little or no response at the flow gauge station); and finally a wet season. The model simulations suggested that water flow paths in Fuirosos were essentially different during wet and dry conditions. Several mechanisms are thought to explain the complex non linear behaviour of this intermittent stream (hence included into the catchment's conceptual scheme):

- During the summer dry season:

  1. The permanently saturated zone (deep aquifer) is disconnected from the stream network.

  2. Water from the permanently saturated zone is lost by transpiration rather than by base flow generation, due to the high water residence time.

- During the wetting-up period:

  3. Water can not percolate to the deep aquifer and it accumulates into the upper weathered bedrock layer forming a transient saturated area or shallow aquifer from which a quick base flow is generated.

  4. In summer, the riparian zone water table may fall significantly; hence the normal hydraulic gradient may reverse with discharge from the river to the riparian zone (inverse flow) in correspondence to the first autumnal storms.

- During the wet season:

  5. The recharge to the permanently saturated zone may occur.

  6. Water table level rises due to large rainfall events and the permanently saturated starts contributing to the stream discharge.

These hypotheses are in agreement with results from previous studies in Mediterranean and semi-arid environments. Pilgrim et al. (1988) and Ye et al. (1998) state that the permanently water table is typically below the streambed and that most rainfall events in arid and semi-arid regions involve relatively small rainfall depth; thus, it is likely that significant recharge of this saturated areas from general infiltration occurs only in extreme events. Caldwell et al. (1998) noted that the amount of water moved by hydraulic lift (which refers to the mechanism by which some vascular plants redistribute soil water) may contribute significantly to the actual evapotranspiration, especially in arid and semi-arid environments, and this mechanism could insure plants tolerance to the summer drought. Ocampo (2006) suggested that the formation of a perched water table is a key hydrological process during the wetting-up period in semi-arid catchments. Finally, Butturini et al. (2002) described the Fuirosos catchment non-linear runoff-rainfall relationship occurring just after the drought period, which makes precipitation episodes falling far below the general trend obtained for the remaining part of the year, and linked this behaviour to the inverse flow (Butturini et al. 2003).

The results obtained considering a semi-distributed catchment scheme (that is the SD4-R model) highlighted the importance of the spatial variability of the evapotranspiration process in semi-arid systems. The simulation of the driest hydrological year (1999-00) was improved significantly only when the HRUs slope aspect and the vegetation coverage were included in the computation of the actual evapotranspiration. This is in agreement with Piñol et al. (1997) that stressed that vegetation in semi-arid systems can be considered a major driver of the annual water balance through transpiration.

Based on the four-response hydrological scheme, three catchment-scale nitrogen models were developed. The N model adopted provides a simplified conceptualization of the soil nitrogen cycle considering mineralization, nitrification, immobilization, denitrification, plant uptake, and ammonium adsorption/desorption. It also includes shallow aquifer nitrification and denitrification processes in the upper part of the weathered bedrock. Moreover, a different soil moisture threshold has been introduced for each soil process to determine activation. The three models increase in their spatial complexity evolving from an initial lumped structure (LU4-N) to a semi-distributed one (LU4-R-N) including the riparian zone along with the four small reservoirs of the catchment. Eventually the LU4-R-N model was evolved to a more complex semi-distributed model (SD4-R-N) including the riparian zone, the four reservoirs and catchment spatial variability in land cover and geology (Bernal et al., 2004, Medici et al., 2008; Medici et al., 2010).

The most important conclusions obtained about the inorganic nitrogen dynamic in the Fuirosos catchment are:

1. The results suggested that all the soil nitrogen processes were highly influenced by the rain episodes and that soil microbial processes occurred in 'pulses' stimulated by soil moisture increasing after rain.
2. The model simulations highlighted the riparian zone as a possible source of nitrate, especially after the summer drought period, but it can also act as an important sink of nitrate due to denitrification, in particular during the wettest period of the year. The riparian zone was indeed a key element to simulate the catchment nitrate behaviour.
3. It was highlighted that in the riparian zone the mechanism of mineralization-nitrification can be essentially different from the rest of the catchment due to the specific moisture condition and different organic matter that can be found there. Namely, our results suggested:
    a. Higher mineralization rate in the riparian area than in the rest of the catchment.
    b. Nitrification seems to occur more continuously in the riparian soil than in the catchment hillslope, which together with the interflow flushing effect can give rise to important stream nitrate concentration peaks.

4. Simulated mineralization seems to be highest immediately after the summer drought period (‘Birch effect’, Birch 1959, 1960, and 1964), when the soil moisture content reaches approximately 50% of the soil field capacity.
5. The SD4-R-N model can reproduce huge pulses of nitrification in the riparian soil just after the summer drought, because of the sudden increase in soil moisture content due to the reverse flux.
6. The results obtained highlighted the nitrification and denitrification processes in the unsaturated weathered granite, below the soil organic horizon, as important processes.
7. Further work is needed to develop better simulations of ammonium storage and transport in the catchment and the link between organic-N and ammonium.

The seven conclusions are in agreement with results from previous researches in Mediterranean and semi-arid environments. The influence that wet-dry cycles have on microbial biomass and inorganic nitrogen processes has been stressed by Van Gestel et al., (1993) and Mummey et al., (1994). Schiwinning et al. (2004a, 2004b) spoke about a ‘pulse dynamic’ in arid and semi-arid ecosystems, considering the rainfall inputs to a dry soil as triggers of a cascade of biogeochemical and biological transformations. Intermittent streams and their associated riparian zone were highlighted as ‘hot spots’ for biogeochemical processes in arid and semi-arid regions and it was observed that Mediterranean riparian soils act as source or sink of dissolved nitrogen depending on the period of the year (McIntyre et al., 2009, Bernal et al. 2008, Butturini et al. 2003). McIntyre et al. (2009) noted that, for a semi-arid intermittent stream, mineralization is reduced under soil moisture conditions close to saturation, while mineralization is increased under moderate saturation. Moreover, in a previous study performed in the soil of the riparian area of Fuirosos, Bernal et al. (2003) reported the highest mineralization rates in autumn. Butturini et al. (2003) pointed out the reverse flux as a possible mechanism responsible for nitrate release in the riparian zone. Finally, Legout et al. (2005), in previous studies of biogeochemical activities in the unsaturated zone of weathered granite demonstrated potential for bacterial activity and biogeochemical reaction in the lower soil horizons associated with lower carbon content. In particular, it was suggested that both nitrification and denitrification are likely to take place in the unsaturated weathered granite below the soil organic horizon.

The progression from the simplest conceptual model (LU4-N model) to the most complex (SD4-R-N model) is reflected by an increase in the number of parameters to be calibrated from 27 to 59. Therefore, the last part of the present work focused on identifying important models parameters and aimed to determine if additional model complexity actually gives a better capability to model the hydrology and nitrogen dynamics of the Fuirosos catchment. To address this issue an extensive regionalised sensitivity analysis based on Monte Carlo simulations was done (GSA or HSY, Whitehead and Young 1979 and Hornberger and Spear, 1980; GLUE, Beven and Binley, 1992). The main conclusions obtained are:

1. The parameters defining the four different catchment hydrological responses were highlighted as influential on discharge simulation, suggesting that any simplification of the hydrological scheme adopted should not be recommended.
2. The thresholds mechanisms introduced to simulate the non linear hydrological and nitrogen behaviour observed in the Fuirosos catchment were always pointed out as influential on models results. This supports their inclusion into the model conceptual scheme.
3. From the point of view of the hydrological modelling, the riparian zone parameters seem to affect only the lowest simulated discharge during the catchment drying-up and wetting-up.
4. From the point of view of the nitrogen modelling, the riparian zone parameters gain importance, in particular riparian local

aquifer nitrification/denitrification processes ($K_{nitr\_aq\_ripz}$ and $K_{denitr\_aq\_ripz}$). Stream-riparian zone system seems to represent an important mechanism to take into account to simulate inorganic nitrogen.

5. For discharge, the number of behavioural outputs decreases with model complexity (which indicates less model degrees of freedom), but the portion of observed data included within the 5% and 95% GLUE bounds gets larger, suggesting increasing models ability to reproduce observed data. In particular:
    a. The results stress that the SD4-R-N model is the only one able to reproduce satisfactorily the three hydrological years simultaneously.
    b. The GLUE band width, obtained considering a single-objective approach, for the SD4-R-N model (the most complex) is narrower than that of LU4-N model (the simplest one). This highlights that the SD4-R-N model is more insensitive to parameters than the LU4-N model, which is a desirable result.
    c. The GLUE band width, obtained considering a multi-objective approach, for the SD4-R-N model is comparable with that of LU4-N model, though it includes a higher percentage of observed data for both discharge and stream nitrate concentration.
6. The number of behavioural outputs for nitrate increases with model complexity. In particular:
    a. In the case of the LU4-R-N model, the riparian zone increases the model's degrees of freedom for nitrate simulations giving more chances to the model to reproduce the observed data. However it also increases the model's bias especially during catchment wetting-up.

    b. In the case of SD4-R-N model, the larger number of behavioural outputs obtained for nitrate can be explained with the improved discharge simulation.
7. Nitrate near-optimum parameters sets generally provided acceptable discharge simulations. On the contrary, discharge best parameters sets did not guarantee acceptable nitrate simulations.
8. A simultaneous calibration of all the most sensitive models parameters was revealed as the best calibration strategy (as suggested also by McIntyre et al. 2005).
9. The number of equally good models (according to the GLUE terminology) decreases enormously when hydrological and water quality are modelled simultaneously. Hence, it suggests that stream nitrate and ammonium concentrations may help to constrain nitrogen-significant hydrological parameters and discard some hydrological mechanisms in favour of others.

In summary, the progressive perceptual approach adopted in this study led from an initial lumped structure (LU4-N) to a final more complex semi-distributed model (SD4-R-N). This process involved increasing the number of parameters and brings about a general improvement of the efficiency indexes. The results obtained highlighted the most complex structure (SD4-R-N) as the most appropriate one representing the non-linear behaviour of this small Mediterranean catchment. The results of the temporal and spatial validation as well as the ones of the sensitivity analysis show that the possible over-parameterization of this model can be accepted.

5.2 Future research lines

There is a very important corollary to modelling as a process of learning about places in this way. Such a learning process cannot proceed without continued collection of data that should imply both the continued monitoring of the systems of interest and more directed, cost-effective, local measurement campaigns to learn more about places of particular significance.

Hence, requirements for future work:

1. Collecting more measurements that will allow for different hypothesis and assumptions to be tested in a way that eliminates some of the set of feasible or behavioural models.
    a. Collecting more data should also focus on improving the understanding of the storage, transport and transformation of ammonium in the environment.
2. Testing the developed models in other Mediterranean catchments, to understand the relevance of the important mechanisms highlighted in this work.
3. Uncertainty analysis of model predictive capabilities.

6

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