contaminación de las aguas subterráneas donde en numerosas ocasiones se superan los 50 mg NO_3^-/l impuestos por la Directiva 91/676/CEE. A pesar de que la cantidad de agua infiltrada sea mayor durante el ciclo del trigo, periodo invernal, las pérdidas de nitrógeno por lixiviación son menores que en el caso de la remolacha. Según los datos aportados por el modelo para la remolacha y trigo, se habrían lixiviado 32 y 12 kg N/ha, respectivamente. Estas cantidades suponen un 9 y 4 % del total de N aportado al suelo. Siendo, por tanto, la remolacha el cultivo que mayores pérdidas de nitrógeno presenta. La mayoría del nitrógeno aportado, entre un 52 y un 73 % dependiendo del cultivo, pertenece a los abonados, mientras que el resto corresponde a la reserva inicial del suelo y a la mineralización del humus.

En otros trabajos anteriores (Jégo et al. 2008) ya se obtuvieron importantes conclusiones de la simulación de dos cultivos, patata y remolacha, en otras parcelas de la llanada alavesa. Incluso bajo las mismas condiciones de fertilización e irrigación, se observó que la concentración de nitrato (mg/l) en las aguas de drenaje bajo el cultivo de patata era muy superior a la de remolacha. En este caso se recomendaba plantar un cultivo intermedio entre la patata y la remolacha con el fin de minimizar el riesgo de contaminación por lixiviación de nitrato a las aguas subterráneas. En el caso de los cultivos consecutivos, remolacha y trigo, aquí expuestos, se observa que con fertilizaciones casi iguales es la remolacha el cultivo que mayor cantidad de nitrato lixivia y no sólo durante los regadíos. La rotación de estos dos cultivos, además de ser una práctica muy extendida en toda la llanada alavesa, resulta ser beneficiosa, ya que el nitrógeno acumulado en el suelo después de la cosecha de la remolacha es aprovechado por el trigo, disminuyéndose enormemente la lixiviación. Se trata de algunos ejemplos de aplicación del modelo STICS, que puede tener una gran potencialidad de uso en zonas agrícolas.

Agradecimientos. Esta investigación ha sido auspiciada por el Departamento de Agricultura del Gobierno Vasco – Eusko Jaurlaritza, y se enmarca en un estudio más amplio sobre la dinámica de los nitratos en el acuífero cuaternario de Vitoria-Gasteiz (proyecto CGL2006-06485 del Ministerio de Ciencia e Innovación, y Grupo Consolidado (GIC07/08-IT-392-07) del Gobierno Vasco-Eusko Jaurlaritza).

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APPLICATION OF A LUMPED NITROGEN MODEL TO A SMALL MEDITERRANEAN CATCHMENT, FUIROSOS (CATALONIA)

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Palabras clave: Mediterranean catchment, Nitrogen cycle, Processes Pulses Behaviour

RESUMEN. *En este trabajo se ha desarrollado un submodelo de simulación de nitrógeno que ha sido acoplado a un modelo hidrológico ya existente, LU4, dando origen al modelo LU4-N para cuencas Mediterráneas. El modelo LU4-N se basa en los principales procesos que entran en juego en el ciclo del nitrógeno en el suelo: mineralización, nitrificación, inmovilización, desnitrificación, absorción por parte de las plantas y el proceso de adsorción/deserción del amonio. Se incluyen además los procesos de nitrificación y desnitrificación en el acuífero superficial colgado. Para cada proceso involucrado en el ciclo del nitrógeno del suelo, se han introducido umbrales de humedad. Los resultados obtenidos apuntan a que la alternancia de estados secos y húmedos, típicos de cuencas Mediterráneas como es la de Fuirosos, parece traducirse en un comportamiento a "pulsos" de los procesos biológicos, desencadenado por los episodios de lluvia. El proceso de validación temporal evidencia algunas lagunas del modelo LU4-N.*

ABSTRACT. *The aim of this work was to couple a nitrogen submodel to an existing rainfall-runoff model LU4, to develop an understanding of the factors and processes controlling nitrogen cycling integrate in Mediterranean systems. The LU4-N model provides a simplified conceptualization of the soil nitrogen cycle considering mineralization, nitrification, immobilization, denitrification, plant uptake, ammonium adsorption and desorption processes. It also includes nitrification and denitrification in the shallow perched aquifer. The model structure includes a soil moisture threshold for all the considered soil biological processes. The results of the model-based assessment suggest that the soil nitrogen cycle in Fuirosos seems to be mainly influenced by the rain episodes that induce catchment re-wetting. Microbial processes occur in pulses stimulated by soil moisture increasing after rain. The temporal validation process of the LU4-N model is discussed.*

1. INTRODUCTION

Mediterranean catchments are characterized by a complex hydrological behaviour that presents high inter and intra-annual variability (Gallart et al., 2002). In particular, such catchments are subjected to severe drought periods, followed by intense rainfall events. As a consequence, soil N processes and leaching of solutes also show a marked seasonality. In previous studies in Mediterranean regions, the important role played by water was identified in terms of the flushing effect on nutrients and the impact of soil moisture on soil microbial cycles (Austin et al., 2004, Schwinning et al., 2004a). Birch was one of the first to observe it, demonstrating that rapid mineralization follows rewetting of dry soil and the subsequent nitrate release (Birch, 1964). This is now known as the "Birch effect". Many other authors stressed the influence the wet-dry cycles have on microbial biomass: Mummey (1994) observed that denitrification occurs in pulses stimulated by the re-wetting of soil after rains; Serrasolses (1999) showed that nitrification is limited by soil moisture. Schiwinning (2004b) considered the rainfall inputs to a dry soil as pulses that trigger a cascade of biogeochemical and biological transformations. There are still few studies in Mediterranean catchments compared with those in temperate or tropical ones and there is still a need for accurate evaluation of nutrient loads during floods events or over annual periods (Chu Y., et al. 2008). Therefore, further investigation is needed to gain insight into the integration of processes governing the N cycle in these regions. To this end, the object of this research was to develop a process-based model to test hypotheses regarding the hydrological and nitrogen functioning of a small Mediterranean forested catchment, the Fuirosos (Catalonia, Spain). A previous analysis of this catchment with the process-based INCA-N model (Wade et al., 2002) suggested that some key mechanisms to match both the hydrology and nitrate behaviour were missing in the INCA-N model conceptualization (Bernal et al., 2004). The study of previous research results allowed a gradual increase in the perceptual understanding of the catchment. This led to the development of a new conceptual hydrological model LU4 (Medici et al., 2008). This model was eventually extended through the inclusion of processes representing the inorganic nitrogen cycle, following the basic INCA-N philosophy, to create a new model of nitrogen dynamics LU4-N capable of application in Mediterranean systems. The development and application of the model is reported in this paper.

2. STUDY CASE AND DATABASE

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 the Catalan Littoral Range, near Barcelona (Spain) and it is a tributary of the Tordera River. Its drainage area is approximately 13 Km^2. The catchment is an almost pristine, undisturbed forested watershed, with little agricultural activity and no urban areas. The climate is typically Mediterranean, with temperature raging from a monthly mean of 3°C in January to 24°C in August. Winter temperatures below 0°C are infrequent. During the complete observed period, the mean annual precipitation at Fuirosos is about 750 mm (Medici et al., 2008). The first hydrological year (1999-2000) 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. The observed number of days during which the Fuirosos stream is completely dry ranges approximately between 76 (summer 2000) and 98 (summer 2001). 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 Figure 1. At the valley bottom there is an identifiable alluvial zone, where a well-developed riparian area flanks the Fuirosos stream channel. 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. The discharge observed period is from 13/10/1999 to 30/06/2003. Moreover, the database included average daily nitrate (NO_3) streamwater concentrations corresponding to the outlet of the catchment during 1999-2003 and average daily ammonium (NH_4) concentrations during 1999-2002. For a compete description of the Fuirosos chemical water analyses see Bernal et al., 2004 and 2005.

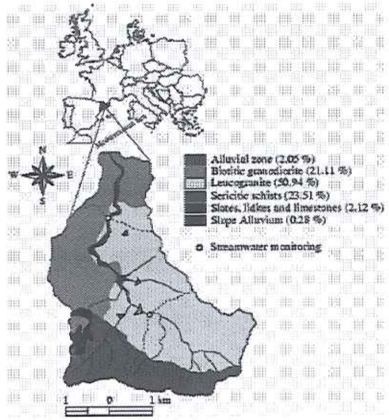

Figura 1. Geographical location of the Fuirosos catchment (Catalonia, NE Spain). Lithological units are shown in different shadings.

3. LU4-N MODEL DESCRIPTION

The LU4 hydrological model (Lumped Model – 4 different hydrological catchment responses), which is presented in detail in Medici et al., 2008, was extended through the inclusion of processes representing the inorganic nitrogen cycle, considering in particular the specific nitrogen dynamics observed in previous studies of Mediterranean catchments. The soil nitrogen cycle conceptual model includes the mineralization process, non-biological nitrate fixation (as a zero order kinematic equations), nitrification process, ammonium bacterial immobilisation, ammonium and nitrate plant uptake, abiotic absorption and denitrification (as first order kinematic equations). A perceptual model which shows key nitrogen stores and pathways is shown in Figure 2. All the processes are corrected by a soil moisture factor ($S_{1\_process}$) and a temperature one (TF), as previously suggested by Whitehead (1998). Moreover, for each soil N process a soil moisture threshold (U) has been introduced, which determines the related process behaviour. For instance, the soil moisture factor for the mineralization process ($0 \le S_{1\_Miner} \le 1$) is calculated as follow:

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

where: H_1 is the actual static storage water content (mm); H_u^* is the maximum static storage water content (mm); IA are the initial abstractions (interception and water detention in puddles) which where estimated approximately 19 mm day^{-1}; t is the time step (day) and U_{Miner} is the soil moisture threshold for mineralization (%), which is expressed as a percentage of H_u^*. According to eq. 1, the S_{1_Miner} factor presents a triangular shape with an "optimum" when the soil moisture content is equal to U_{Miner} (expressed in mm). In this case, the mineralization processes would be described as follow:

$$\left(M_{NH_4}\right)_{Miner.} = K_{Miner} \cdot S_{1\_Miner} \cdot TF \qquad (2)$$

where: M_{NH4} is the ammonium mineralized mass (kg km^{-2} day^{-1}); K_{miner} is mineralization rate constant (kg ha^{-1} day^{-1}) and TF is temperature factor Whitehead (1998). For the rest of processes, the respective soil moisture factors are computed according the following general expression:

$$S_{1\_process} = 0 \quad if \quad 0 \le H_1(t) - IA \le U_{process} \left(\le H_u^* - IA\right)$$
$$S_{1\_process} = \frac{\left(H_1 - IA - U_{process}\right)}{\left(H_u^* - IA - U_{process}\right)} \quad if \quad U_{process} < H_1(t) - IA \le H_u^* - IA \qquad (3)$$

where: $U_{process}$ is the generic soil moisture threshold for any soil process; $S_{1\_process}$ is the soil moisture factor for any soil process.

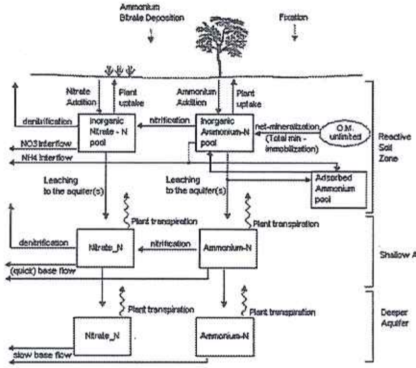

Figure 2. Nitrogen cycle in the soil and aquifers systems for the LU4-N model (modified form Whitehead et al. 1998)

As suggested by Bernal (2004), the adsorption/desorption process was also included in the LU4-N model. In this case, the mass of NH_4 adsorbed in the soil is computed as a fraction of the total dissolved NH_4 carried out by interflow and percolation flow. A daily maximum adsorbed NH_4 amount has been introduced as a parameter to be calibrated. Concerning the aquifer storages included into the LU4 model, it was assumed that the only relevant N processes in the shallow aquifer compartment are nitrification and denitrification (Figure 2). Moreover, an uptake process associated with the transpiration flux was included form both shallow and aquifer storages. It depends on the actual NH_4 and NO_3 concentration in the aquifers, on the amount of water transpirated by plants and finally on the annual maximum solute uptake value.

4. CALIBRATION AND VALIDATION PROCESSES RESULTS

The N-model calibration process was carried out using the calibrated hydrological model parameters from a previous study by Medici et al. (2008), so the nitrogen related parameters only were calibrated. The total number of parameters taken into account was 19, plus 7 initial conditions (Table 1). The calibration was carried out by an automatic process (Evolver 4.0 for Excel {32-bit}) and then by manual adjustment of the parameters to check the model behaviour. Observed and simulated mean daily nitrate concentrations for the calibration period (13/10/1999 to 22/08/2002) are shown in Figure 3a. The Nash & Sutcliffe index (E) for the whole period was approximately 0.46, while for the first, second and third years are respectively: negative, approximately 0.55 and 0.41. The Root Mean Square Error (RMSE) index for the three years was approximately 0.44. The corresponding E indexes for the hydrology were respectively: 0.7 for the whole period, 0.6 for the first and second year and approximately 0.74 for the third year.

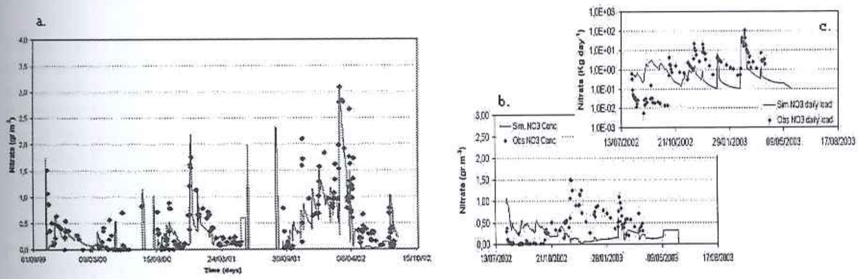

Figure 3. LU4-N model outputs (solid line) and observed nitrate concentration (black diamonds) a) for the three years calibration period (10/99-08/02); b) for the validation period (08/02-30/06); c) observed and simulated daily nitrate loads for the validation period (08/02-30/06).

Concerning the ammonium, it was not possible to achieve any positive E index, which means that the LU4-N model could not reproduce satisfactorily the NH_4 concentration daily behaviour. Though, the RMSE index for the ammonium calibration period was approximately 0.06, which means that at least it was possible to represent the correct average ammonium concentration observed in the streamwater. The simulated nitrogen annual processes rates were consistent with measured rates from studies done in similar catchments (Table 2). From this model-based assessment it is apparent that the soil nitrogen cycle seems to be largely influenced by the rain episodes that induce catchment re-wetting. According to the LU4-N model conceptualization microbial processes occur in pulses, stimulated by soil moisture increasing after rain (Fig. 4). Namely, simulated nitrification, immobilisation and denitrification were allowed to occur only after exceeding the soil moisture threshold that equates to a 30% water storage content (H_u^*), which can be considered as water that is retained in the soil by capillary suction and adsorption (Table 1). In particular, when the simulated soil moisture is not limiting, nitrification occurs

in the model (as well as denitrification and immobilization) and causes a pulse of nitrate. This is due to the nitrification of NH_4 accumulated in soil and its subsequent flushing. Simulated mineralization appears to occur at an optimum rate when the simulated soil moisture content (H_1) is around 40% of H_u^*. This corresponds to the catchment wetting-up period (September-November) (Figure 4). As such, the ammonium accumulated in soil during the dry and transition period is rapidly transformed into nitrate as soon as the right soil moisture increases so that nitrification occurs (U_{nitr}). In general, this happens when the wet period starts so it leads to significant nitrate flushing during winter, when plants are unable to absorb the nutrient produced by the nitrification process, as previously suggested by Bernal (2005)

Table 1. Calibrated parameters description and values for the LU4-N model

	Parameters	Description		Calibrated values
1	K_{Miner}	Mineralization rate	[Kg ha^{-1} day^{-1}]	0.51
2	Knitr	Nitrification rate	[day^{-1}	1.0
3	Kdenitr	Denitrification rate	[day^{-1}]	0.08
4	Kimm	Immobilization rate	[day^{-1}	0.15
5	KupNO3	Nitrate plant uptake rate	[day^{-1}	93.6
6	KupNH4	Ammonium plant uptake rate	[day^{-1}]	90.1
7	Kdenitr_aquif	Shallow aquifer denitrification rate	[day^{-1}]	0.06
8	Knitr_aquif	Shallow aquifer nitrification rate	[day^{-1}]	1.84
9	Kads	Ammonium soil adsorption rate	[day^{-1}]	0.88
10	Kdes	Ammonium soil desorption rate	[day^{-1}]	0.05
11	Umin	Mineralization soil moisture threshold	(%)	48.2
12	Unitr	Nitrification soil moisture threshold	(%)	57.2
13	Udenitr	Denitrification soil moisture threshold	(%)	89.7
14	Uimmob	Immobilization soil moisture threshold	(%)	41.6
15	C9	Maximum temperature difference	(°C)	6.15
16	MaxAdsNH4	Daily max. NH_4 adsorption	[kg day^{-1} km^{-2}]	14.52
17	MaxUPNH4	Annual max. NH_4 uptake	[Kg ha^{-1} day^{-1}]	90.11
18	MaxUPNO3 (1)	Annual max. NO_3 uptake (December, January and February)	[Kg ha^{-1} day^{-1}]	21.63
19	MaxUPNO3 (2)	Annual max. NO_3 uptake for the rest of the year	[Kg ha^{-1} day^{-1}]	118
Initial conditions (Kg Km^{-2})				
20	$NH4_{ads\_in}$	Adsorbed Soil NH_4		2.72
21	$NH4_{in}$	Dissolved Soil NH_4		26.58
22	$NO3_{in}$	Soil NO_3		64.44
23	$NH4_{sh\_aq\_in}$	Shallow aquifer NH_4		0.01
24	$NO3_{sh\_aq\_in}$	Shallow aquifer NO_3		0.01
25	$NH4_{deep\_aq\_in}$	Deep aquifer NH_4		11.33
26	$NO3_{deep\_aq\_in}$	Deep aquifer NO_3		2.27

For the temporal validation, the period from August 2002 to August 2003 was considered. Even if the monthly E index was around 0.8 (indicating that model ability in reproducing at least the seasonal trend), the result obtained was not satisfactory, since the daily nitrate E indexes for the concentration was negative (Figure 3b). The corresponding E index for the hydrology is around 0.4.

Table 2. Nitrogen annual process rates

N Processes	Measured values [Kg ha^{-1} day^{-1}]*	Sim. values [Kg ha^{-1} day^{-1}]
Net mineralization	32.4 – 80.1	62.9
Net nitrification	4.4 – 7.5	6.26
Immobilization	0.08	4.83
Nitrate uptake by vegetation	10.3 - 58	13.07
Ammonium uptake by vegetation	53 – 80.5	58.94

*After Bernal et al., 2004

5. DISCUSSION

The LU4-N model performance for the calibration period can be considered satisfactory, in particular in comparison with the results obtained with the INCA-N model (Bernal et al., 2004). The LU4-N model is able to reproduce the observed ratio between mineralization and nitrification (M:N≅10:1; Table 2) characteristic of Mediterranean regions, which has been shown to be around 10:1 (Serrasolses et al., 1999).

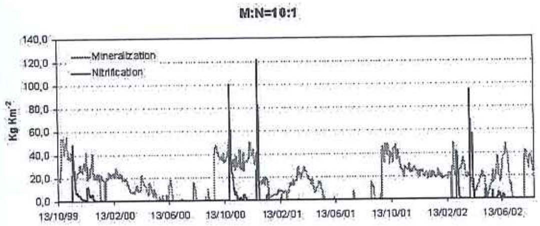

Figure 4. Mineralization : Nitrification ratio (M:N) for the whole period with the LU4-N model. The graph shows the "pulses" of nitrification triggered by the rainfall episodes.

The ability of the LU4-N model to reproduce the observed NO_3 stream concentration for the three year calibration period suggests that the key factors and processes controlling the hydrological and N behaviour are included within the model conceptual scheme and that their mathematical representation seems reasonable. However, the temporal validation process call for caution when considering the result obtained, even if just one year for the validation may not be sufficient to accept or reject the model conceptualization, especially taking into account the hydrological model error propagation. Therefore, it is necessary to use longer temporal series of data that include the higher intra annual-variability typical of these areas to determine if the model is able to represent the catchment nitrogen dynamics. The validation results show that the model generally underestimates NO_3 daily concentrations and loads (Figure 3b and 3c) during periods when the discharge is well simulated, which means that the simulated amount of NO_3 in soil that can be exported is too low. This can be related to many different factors, i.e. high nitrate uptake rate or mineralization/nitrification dynamic. A sensitivity analysis highlighted the mineralization soil moisture threshold (U_{Miner}) as a key factor influencing model results. The value adopted by U_{Miner} changes the relation between mineralization and nitrification, shifting the timing of when NH_4 is available for other processes (i.e. nitrification that would increase the soil nitrate content). Also the nitrification soil moisture threshold (U_{nitr}) and the mineralization constant rate (K_{Miner}) were highlighted as very sensitive parameters. Therefore, it may mean that a better spatial description of the mineralization processes is required rather than a lumped one. In other words, considering the mineralization and nitrification processes rate constants as specific for some particular area rather than uniform for the whole catchment may improve the model performance. To this end, intermittent streams and their associated riparian zone have been highlighted as 'hot spots' for biogeochemical processes in arid and semiarid regions (McIntyre et al., 2009) and Bernal (2005) suggested that during the transition period mineralization activity may be highly influenced by recent litterfall especially in the riparian zone (Hedin et al., 1995). Butturini (2003) in a previous research found at Fuirosos that in the stream edge zone nitrate release predominated over depletion and suggested the unsaturated riparian organic soil layer as a source of nitrate. For these reasons, the role played by the riparian zone should be taken into account for an appropriate simulation of nitrate and ammonium dynamics, even if it is well know that that adding model components and parameters to reproduce specific aspects of catchment behaviour does not necessarily lead to better results.

6. CONCLUSION

The results show that in Fuirosos the nitrogen behaviour is strongly influenced by the soil moisture which is highly variable within and between years. Rainfall inputs to the dry soil seem to act as pulses that trigger biogeochemical and biological transformations. The LU4-N model shows its ability to
reproduce the nitrate behaviour for the calibration period but the temporal validation result was not satisfactory, suggesting that further work is needed to capture the characteristics of this Mediterranean catchments. Several authors (Bernal et al., 2007; McIntyre et al., 2009) note the importance of the riparian

zone as a "hot spot" and 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, the next step will be to progress the LU4-N model to a simple semidistributed structure model splitting the catchment into two representative hydrological units (HRU): 1) the riparian zone that represents approximately 0.5% of the total catchment area and 2) the rest of the catchment. Indeed, this would keep still reasonable the total number of model parameters, but it would give a better representation of the catchment key processes governing nitrate behaviour.

Ackowledgements. This study was supported by a Formación de Personal Investigador (FPI) grant and founds provided by the Generalitat Valenciana, Conselleria d'Educació.

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CARACTERIZACIÓN DEL CAUDAL BASE EN ZONAS DE ALTA MONTAÑA A PARTIR DE UN ANÁLISIS ESTACIONAL DE RECESIONES

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Palabras clave: Caudal base, Análisis de recesión, Concatenación, Modelo hidrológico

RESUMEN. *El estudio del caudal base resulta esencial en la caracterización y cuantificación de recursos hidrológicos de zonas montañosas. En este sentido, el análisis de curvas de recesión proporciona una valiosa información referente a la respuesta de estos aportes y las características medias de los acuíferos, cuando se emplean metodologías que seleccionan y sintetizan fragmentos de recesión en una sola curva, la Curva de Recesión Maestra (CRM), y se comparan los resultados con recesos estivales con el fin de establecer relaciones entre las respuestas. Este procedimiento es clave en la configuración y calibrado de un modelo de aportaciones de caudal base que se integre en un modelo hidrológico global. En este trabajo se ha aplicado esta metodología en tres subcuencas pertenecientes a Sierra Nevada (Granada), en entorno mediterráneo. Los resultados han permitido identificar las diferentes respuestas del caudal base y modelar estas aportaciones, verificando la validez del método propuesto.*

ABSTRACT. *The study of baseflow in mountainous areas is essential in the characterization and quantification of water resources in mountainous areas. In this sense, the recession analysis provides information on the type of response of the subterranean systems and on the average characteristics of aquifers, when methodologies which select and combines fragments of recession into a single curve, the Master Recession Curve (MRC), are applied and the study of recessions during the dry season are used to compare and validate the results obtained. This procedure is essential in the configuration and validation of a hydrological model which include baseflow contributions. In this work, this methodology has been applied to three sub-basins belonging to a high altitude mountain basin in Sierra Nevada (Granada). The results show the existence of two different responses of baseflow and allow the modeling of these flows, checking the validity of the proposed methodology.*

1. INTRODUCCIÓN

Dependiendo de la procedencia de los recursos hidrológicos, la escorrentía puede definirse de una manera muy simplificada como la suma de dos componentes; escorrentía directa y la escorrentía subsuperficial y base correspondiente a la fracción de agua que, una vez infiltrada, recarga y circula a través del suelo y los acuíferos descargando posteriormente su almacenamiento en los ríos, lagos o en el mar. Este segundo tipo de aportes, de respuesta más lenta y continuada se denomina flujo base o **caudal base** y su importancia es crucial desde el punto de vista cuantitativo y cualitativo de los recursos del sistema hidrológico.

La heterogeneidad en el origen del caudal base (Hall, 1968) obliga a analizar cada sistema separando cada uno de los procesos involucrados. Para ello, es preciso diferenciar aquellas aportaciones procedentes de la zona no saturada del suelo. Este flujo recibe el nombre de flujo intermedio (*interflow*) o caudal lateral y Beven (1989), lo define como un flujo cercano a la superficie dentro del perfil del suelo y el marco temporal asociado al evento,