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The influence of Mediterranean riparian forests on stream nitrogen dynamics: a review from a catchment perspective

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ABSTRACT

The influence of Mediterranean riparian forests on stream nitrogen dynamics: a review from a catchment perspective

Riparian zones are considered natural filters of nitrogen (N) within catchments because they can substantially diminish the exports of N from terrestrial to aquatic ecosystems. However, understanding the influence of riparian zones on regulating N exports at the catchment scale still remains a big challenge in ecology, mainly because upscaling plot scale results is difficult, as it is disentangling the effects of riparian, upland, and in-stream processes on stream water chemistry. In this review, we summarize previous studies examining key hydrological and biogeochemical processes by which Mediterranean riparian zones regulate catchment water and N exports. We focus on Mediterranean regions because they experience a marked climatic seasonality that facilitates disentangling the close link between climate, riparian hydrology, and stream N exports. We show that Mediterranean riparian soils can be hot spots of N mineralization and nitrification within catchments given their relatively moist conditions and large stocks of N-rich leaf litter. Extremely large nitrification rates can occur during short-time periods (i.e. hot moments) and lead to increases in stream N loads, suggesting that riparian soils can be a potential source of N to adjacent aquatic systems. Moreover, riparian trees can contribute to decrease riparian groundwater level during the vegetative period, and promote reverse fluxes from the stream to the riparian zone. During periods of high hydrological retention, stream water exports to downstream ecosystem decrease, while stream water chemistry is mostly determined by in-stream processes. Riparian tree phenology can also affect catchment N exports by shaping the temporal pattern of both light and litter inputs into the stream. In spring, light enhances in-stream photoautotrophic N uptake before riparian leaf-out, while riparian leaf litter inputs promote in-stream N mineralization in summer and fall. Finally, we illustrate that the impact of Mediterranean riparian zones on stream hydrology and biogeochemistry increases along the stream continuum, and can ultimately influence catchment N exports to downstream ecosystems. Overall, findings gathered in this review question the well-established idea that riparian zones are efficient N buffers, at least for Mediterranean regions, and stress that an integrated view of upland, riparian, and stream ecosystems is essential for advancing our understanding of catchment hydrology and biogeochemistry.

Key words: Soil nitrogen cycle, evapotranspiration, riparian canopy, catchment hydrology, in-stream biogeochemical processes.

RESUMEN

La influencia de los bosques de ribera mediterráneos en la dinámica del nitrógeno en los ríos: una revisión desde una perspectiva de cuenca

Las zonas de ribera son filtros naturales de nitrógeno (N) y disminuyen substancialmente los aportes terrestres de N que llegan a los ríos. Sin embargo, entender cómo las riberas regulan el exporte de N a escala de cuenca es aún un reto porque extrapolar los estudios de parcela a escala de cuenca es difícil, así como también lo es discernir la contribución de los procesos que *ocurren en las cabeceras, riberas, y en los propios ríos en la química del agua. En esta revisión, se resumen distintos estudios que examinan los procesos hidrológicos y biogeoquímicos mediante los cuales los bosques de ribera mediterráneos regulan el exporte de agua y N aguas abajo. La revisión se centra en las zonas mediterráneas, ya que su marcada estacionalidad climática permite discernir la estrecha relación entre el clima, la hidrología de la ribera y las exportaciones de N. Los estudios analizados muestran que los suelos ribereños pueden ser puntos calientes de mineralización y nitrificación dentro de las cuencas mediterráneas gracias a las condicionas relativamente húmedas del suelo y a la hojarasca enriquecida en N. Tasas de nitrificación extremadamente altas suceden puntualmente (i.e. momentos calientes) e incrementan las exportaciones de N; sugiriendo que los suelos ribereños son fuentes de N para los ríos. Además, los árboles ribereños contribuyen a la disminución del nivel freático durante el periodo vegetativo y promueven el movimiento de agua del río hacia la ribera. Durante épocas de alta retención hidrológica, el exporte de agua disminuye y su señal química depende principalmente de los procesos biogeoquímicos fluviales. El dosel ribereño también puede afectar al exporte de N aguas abajo, ya que controla las entradas de luz y hojarasca. En primavera, la asimilación fotoautotrófica de N aumenta justo antes de que las hojas broten, mientras que los aportes de hojarasca pueden incentivar los procesos de mineralización en verano y otoño. Finalmente, la influencia de las riberas mediterráneas sobre la hidrología y biogeoquímica del río incrementa a lo largo del río y modula el exporte de N a escala de cuenca. En conjunto, los resultados de esta revisión cuestionan la idea de que los ecosistemas de ribera mediterráneos son filtros eficientes de N; y ponen de manifiesto la importancia de integrar el funcionamiento de los bosques de cabecera, las zonas de ribera y los ríos para avanzar en el conocimiento sobre la hidrología y biogeoquímica a escala de cuenca.*

Palabras clave: *Ciclo del nitrógeno, suelos forestales, evapotranspiración, dosel ribereño, hidrología de cuenca, procesos biogeoquímicos fluviales.*

INTRODUCTION

During the last decade, anthropogenic activities have doubled the amount of available nitrogen (N) in freshwater ecosystems, leading to several environmental problems such as eutrophication, acidity, toxicity, or biodiversity declines (Vitousek *et al.*, 1997; Schlesinger, 2009). The environmental issues derived from N excesses may be intensified in the future because increased warming and dryness would probably reduce water availability as well as the dilution capacity of fluvial ecosystems (Cooper *et al.*, 2013). Within catchments, riparian buffer strips have been considered as an economical environmentally efficient tool for protecting freshwaters from diffuse N pollution because they can contribute to decrease N fluxes from terrestrial to aquatic environments (McClain *et al.*, 2003; Vidon *et al.*, 2010).

The high capacity of riparian zones to reduce terrestrial dissolved inorganic N (DIN) inputs derives from the topographic, hydrologic, and biogeochemical conditions at their unique interface location between upland and streams. Flat topographies, permanent upland-riparian hydrologic connectivity, shallow riparian groundwater tables, and carbon (C) enriched soils usually favor ammonium (NH_4^+) and nitrate (NO_3^-) removal via denitrification and biological uptake (Pinay *et al.*, 2000; Dosskey *et al.*, 2010). Conversely, riparian zones that are seasonally disconnected from uplands have large annual water table drawdowns that dry out riparian soils (Ocampo *et al.,* 2006; Vidon & Hill, 2004), which enhance microbial N mineralization and nitrification and increase soil NO_3^- availability (Harms & Grimm, 2010; Duncan *et al.*, 2015). In some cases, the hydrologic disconnection between uplands and riparian systems promote the loss of water from the stream to the riparian zone (i.e. stream hydrological retention) (Rassam *et al.*, 2006), which can favor the assimilation of stream DIN by biota at the stream-riparian edge, and consequently, decrease DIN concentrations (Schade *et al.*, 2002; Dent *et al.*, 2007; Bernal & Sabater, 2012). Therefore, the variability in space and time of soil moisture conditions, groundwater table elevation, and water flow paths can substantial impact the fate and transport of N through riparian zones.

Mediterranean systems (Med systems from here on) are a unique natural laboratory to understand the close link between catchment hydrology and riparian N buffer capacity because they are characterized by a marked seasonal pattern in both temperature and precipitation. Med regions are subjected to a seasonal alternation of wet (spring), dry (summer), and rewetting (early-fall) periods, which can affect N removal in riparian zones by altering the riparian groundwater table elevation as well as the hydrological connectivity between uplands, riparian, and stream systems (Fig. 1). During rewetting events, shallow groundwater levels and moist soils can promote pulses of N mineralization, assimila-

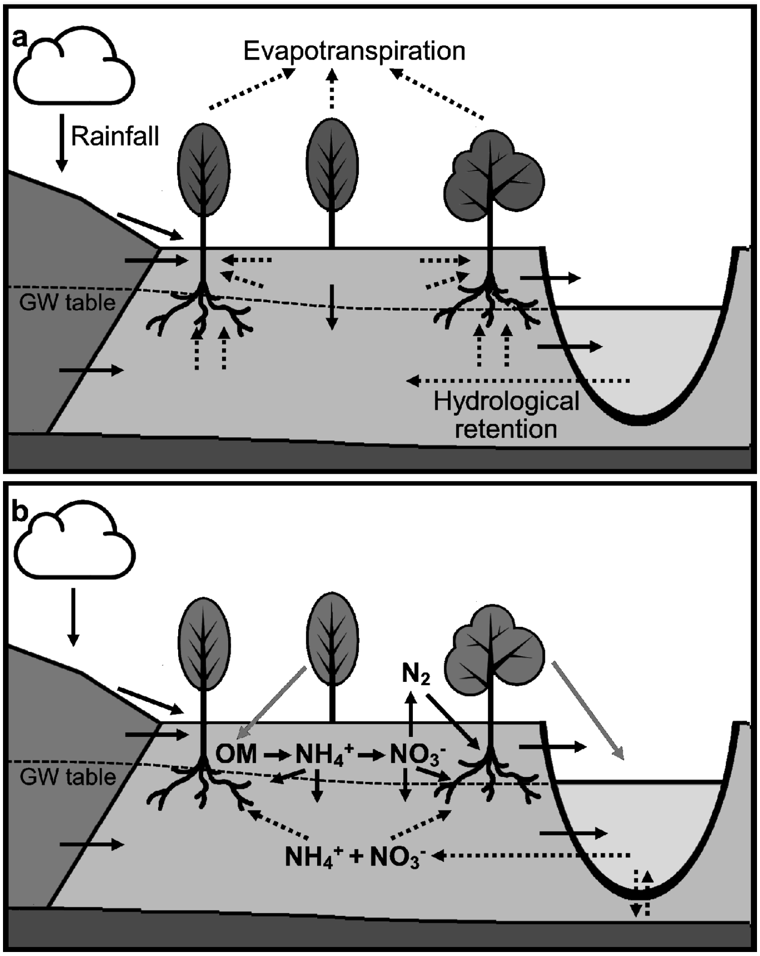

Figure 1. Main fluxes of (a) water and (b) nitrogen in Mediterranean riparian forests. During rewetting events (solid arrows), water inputs from rainfall and uplands increase groundwater levels and moist the soil. Increased water availability enhances soil N processing (mineralization, nitrification, biological assimilation, and denitrification) as well as the transport of inorganic nitrogen from riparian soils to streams. During dry periods (dashed arrows), riparian evapotranspiration promotes the movement of water from the stream to the riparian zone (i.e. stream hydrological retention), which can favor biological assimilation and denitrification at the stream-riparian interface. Moreover, the riparian canopy is an important source of organic nitrogen to both riparian soils and streams in summer and fall (gray arrows). *Principales flujos de (a) agua y (b) nitrógeno en los bosques de ribera mediterráneos. Tras los eventos de lluvia (líneas solidas), las entradas de agua de lluvia y de las zonas de cabecera incrementan el nivel freático y humedecen el suelo. El incremento en la disponibilidad de agua favorece el ciclado del nitrógeno en el suelo (mineralización, nitrificación, asimilación biológica y desnitrificación), así como el transporte de nitrógeno inorgánico desde el suelo ribereño hasta el río. Durante los períodos secos (líneas discontinuas), la evapotranspiración de los árboles ribereños promueve la entrada de agua del río hacia la ribera (i.e. retención hidrológica), la cual favorece los procesos de asimilación de nitrógeno y desnitrificación en la interface río-ribera. Además, la hojarasca de los árboles puede ser una fuente importante de nitrógeno orgánico para la ribera y el río en verano y otoño (líneas grises).*

tion, and leaching, which can have a direct effect on N pools not only in riparian soils, but also in riparian groundwater and stream compartments (Butturini *et al*., 2003; Lupon *et al*., 2016a). At the other end, low moisture conditions can limit soil biological activity during summer, reducing DIN removal and favoring the storage of N in riparian soils (Butturini *et al*., 2003). Moreover, stream hydrological retention induced by riparian evapotranspiration (ET) can decrease stream water export and enhance DIN retention at the stream-riparian edge (Bernal *et al.,* 2013; Vazquez *et al.,* 2013; Lupon *et al*., 2016b). This dual behavior of Med riparian zones between the wet and dry seasons pinpoints that their buffer capacity is extremely vulnerable to changes in climate, and therefore, future alterations in precipitation and temperature regimes may severely affect the magnitude and temporal pattern of N exports from Med continental systems.

Much of our current understanding of riparian hydrology and biogeochemistry in Med-regions has been obtained from studies carried out at plot or reach scale. However, the capability of riparian zones to modify catchment N exports is still poorly understood, limiting our ability for an integrated conservation and management of these ecosystems within the landscape (Vidon *et al*., 2010; Pinay *et al*., 2015). Quantifying the role of riparian zones at catchment scale is complex and not always easy to achieve because stream water chemistry integrates biogeochemical processes co-occurring within upland, riparian, and fluvial ecosystems. Furthermore, processes occurring in different landscape units mutually influence each other, and thus, both uplands and stream can affect the buffer capacity of riparian zones by regulating the amount of water, carbon, and DIN entering to riparian zones (Pinay *et al*., 2000; Dent *et al*., 2007). For instance, previous studies have shown that the capability of riparian zones to regulate catchment N export may change from headwaters to the valley bottom as a result of changes in upland-riparian hydrologic connectivity (Ocampo *et. al.,* 2006; Jencso *et al*., 2009) and stream hydrological retention (Covino *et al*., 2010; Montreuil *et al*., 2010). Therefore, an integrated view of hydrological and biogeochemical processes occurring across landscape units within the catchment is needed to assess the potential influence of riparian processes on stream N dynamics at catchment scale (Bormann & Likens, 1967).

The present review aims to explore the influence of Med riparian zones on regulating both stream hydrology and N dynamics at catchment scale. To this end, we gleaned different empirical and modelling studies from the literature in order to (i) summarize the current knowledge of N biogeochemistry in Med riparian zones and (ii) discuss their potential implications at catchment scale and within the context of climate change. Specifically, this review focuses on three major processes by which Med riparian zones can shape catchment N exports: (i) the role of soil N transformations on stream N exports during rewetting events, (ii) the influence of riparian tree ET on stream water and N retention during the vegetative period, and (iii) the capability of riparian canopy dynamics to shape stream N processes. The studies summarized here comprise different monitoring strategies and include different catchment pools, which ultimately shed light on the relevance of the riparian system within the upland-riparian-stream context.

RIPARIAN SOILS AS POTENTIAL SOURCES OF N TO STREAMS

Soil microbial activity is essential to understand soil N availability in catchments, especially in those regions experiencing low atmospheric N inputs (Kendall *et al*., 2007). The biogeochemical processes involved in the soil N cycle depend primarily on N and water availability. Soil organic matter can be quickly mineralized to NH_4^+ under either relatively oxic or anoxic conditions, nitrification can only occur in aerated soils (water filled pore space (WFPS) $< 80\%$), and both denitrification and dissimilatory nitrate reduction require saturated soils (WFPS $> 60\%$) (Linn & Doran, 1984). Furthermore, soils that are N-enriched due to natural or artificial N fertilization (i.e. N_2 fixation, atmospheric deposition, agriculture) can hold higher rates of soil

N processes than N-poor soils (Vitousek *et al.*, 1997; LeBauer & Treseder, 2008). Ultimately, the combination of all these processes mediates the amount of inorganic N that is available to be leach out, and consequently, the temporal and spatial patterns of catchment N exports (Goodale *et al.*, 2009; Ross *et al.*, 2012).

Within Med catchments, riparian zones exhibit larger net N mineralization (0.7-2.3 mg N kg^{-1} d^{-1}) and net nitrification rates (0.6-1.5 mg N kg^{-1} d^{-1}) compared to surrounding upland soils (< 0.5 mg N kg^{-1} d^{-1}) (Davis *et al.*, 2011; Smith *et al.*, 2012; Lupon *et al.*, 2016a). Increased microbial N production in Med riparian soils has been attributed to the surplus of organic N from the leaf litter of N_2-fixing species (C:N ratio < 20) and to their relatively wet conditions (WFPS = 40-80%) compared to upland soils (Medici *et al.*, 2010; Lupon *et al.*, 2015). However, denitrification rates are usually low in Med riparian soils (0-0.24 mg N kg^{-1} d^{-1}) as a result of water unsaturated soils (Bernal *et al.*, 2007; Davis *et al.*, 2011; Hinshaw & Dahlgren, 2016). In fact, the contribution of denitrification to N depletion from riparian groundwater is thought to be negligible at annual and seasonal scales (Sabater & Bernal, 2011).

Ultimately, high nitrification and low denitrification rates lead to high soil NO_3^- availability (5-20 mg N kg^{-1}) in Med riparian zones (Bernal *et al.*, 2007; Smith *et al.*, 2012; Lupon *et al.*, 2016a); and thus, Med riparian zones can be considered hot spots of soil microbial N supply within catchments. Noteworthy, the role of riparian zones on whole catchment N budgets can vary widely among biomes. In arid riparian zones, water scarcity (WFPS < 30%) usually limits soil microbial activity, and therefore, the contribution of riparian zones to catchment N production and losses is thought to be small (Harms & Grimm, 2010; Dijkstra *et al.*, 2012). On the other extreme, temperate and tropical systems usually show waterlogged riparian soils (WFPS > 70%) where denitrification rates are enhanced (0.2-0.8 mg N kg^{-1} d^{-1}). Hence, humid riparian zones usually become hot spots of N removal at catchment scale (McClain *et al.*, 2003; Vidon *et al.*, 2010).

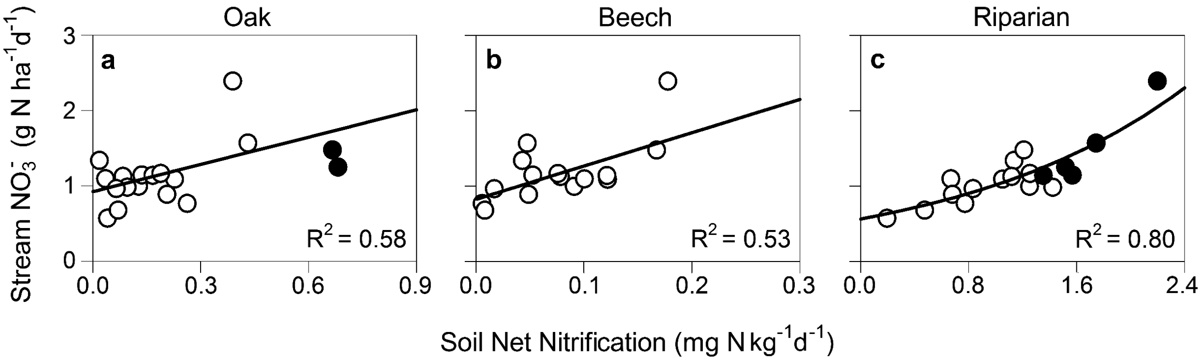

Figure 2. Relationship between soil net nitrification rates and stream nitrate export (expressed by catchment area) for (a) oak, (b) beech, and (c) riparian forests coexisting in a Med catchment of NE Spain. Net nitrification rates and stream nitrate exports were measured simultaneously every 2-4 weeks from March 2010 to February 2011. Black circles represent pulses of net nitrification (i.e. disproportionally high rates compared to the median of the distribution) and solid lines indicate the best fitting model. The influence of nitrification rates on stream nitrate loads differed among forest types; most of the nitrate produced in upland soils was retained within the catchment, while riparian soils were potential nitrogen sources to streams. Adapted from Lupon *et al.* (2016a). *Relación entre las tasas netas de nitrificación en el suelo y las cargas (expresadas por área específica) de nitrato del río para (a) un encinar, (b) un hayedo y (c) un bosque de ribera en una cuenca mediterránea del NE de España. Las tasas netas de nitrificación y las cargas de nitrato del río se midieron simultáneamente cada 2-4 semanas desde Marzo 2010 hasta Febrero 2011. Los círculos negros representan pulsos de nitrificación (i.e. tasas desproporcionadamente más altas que la media de la distribución) y las líneas sólidas indican el modelo de mejor ajuste. La figura muestra que la influencia de las tasas de nitrificación sobre las cargas de nitrato del río difiere entre los bosques: la mayor parte del nitrato producido en los suelos forestales es retenida dentro de la cuenca, mientras que los suelos ribereños pueden ser fuentes potenciales de nitrógeno para los ríos. Figura adaptada de Lupon* et al. *(2016a).*

Soil microbial activity in Med-regions not only vary across forest types, but also over time. Several studies have reported large rates of soil microbial processes immediately after rain events, which can be > 10 fold higher than those observed in the antecedent days (Serrasolses, 1999; Rey *et al.*, 2002). Despite these pulses of microbial N supply may occur during short time

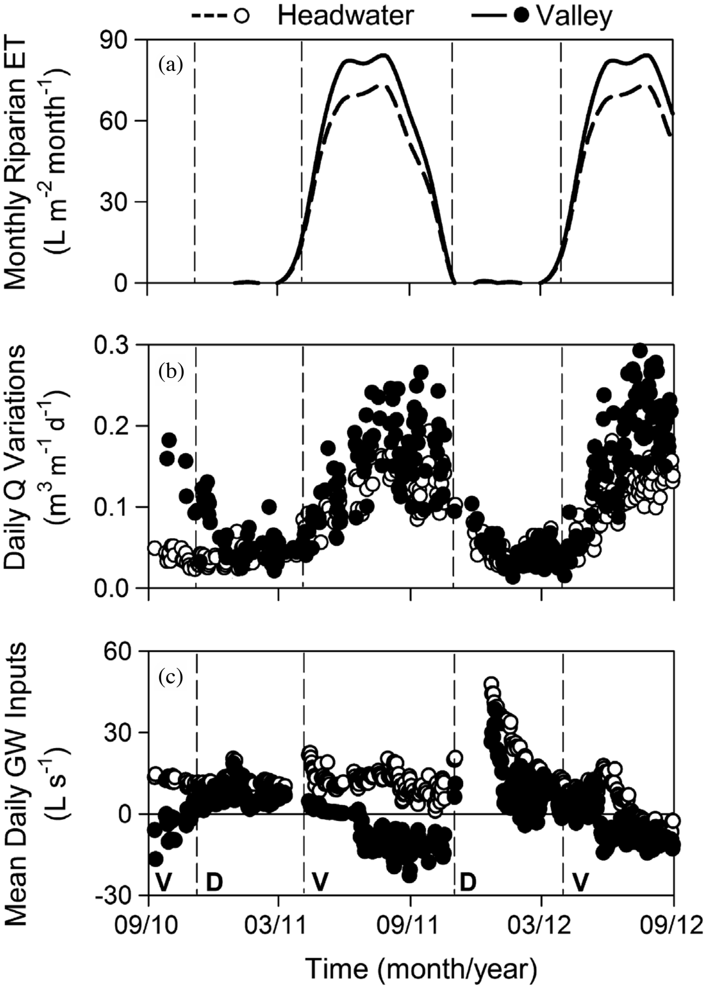

Figure 3. Temporal pattern of (a) monthly riparian evapotranspiration based on sap-flow measurements, (b) daily variations in stream discharge, and (c) mean daily net riparian groundwater inputs for two contiguous reaches during the period 2010-2012. The headwater reach had a poor developed riparian zone (5-10 m wide), while it was well-developed in the valley reach (30 m wide). In panel (c), mean daily groundwater inputs > 0 and < 0 indicate when the stream reach was net gaining and net losing water, respectively. Riparian ET promoted diel discharge variations and stream hydrological retention (i.e. the displacement of water from the stream to the riparian zone), especially in the valley reach, where the riparian zone had higher water requirements. V: vegetative period, D: dormant period. Adapted from Lupon *et al.* (2016b). *Variación temporal de (a) la tasa mensual de evapotranspiración en la ribera medida a partir del flujo de salvia, (b) los ciclos diarios del caudal y (c) las entradas netas de agua freática al río para dos tramos de río contiguos durante el periodo 2010-2012. El tramo de cabecera tenía una escasa zona de ribera (5-10 m de anchura), mientras que ésta estaba bien desarrollada en el fondo del valle (30 m de anchura). En el panel (c), los valores > 0 corresponde a periodos durante los cuales el tramo fluvial recibe agua de forma neta, mientras que los valores < 0 indican lo contrario. La evapotranspiración de los árboles ribereños causó ciclos diarios en el caudal y promovió la retención hidráulica (i.e. la entrada de agua del río hacia la ribera), siendo especialmente notoria en el tramo del fondo de valle, donde la ribera tenía más requerimientos de agua. V: periodo vegetativo, D: periodo durmiente. Figura adaptada de Lupon* et al. *(2016b).*

periods, novel studies suggest that they can contribute up to 25-40% of annual mineralization and nitrification (Lupon *et al.*, 2016a). Moreover, such biogeochemical pulses (or hot moments) can increase catchment N exports because rainfall events are usually associated with a large mobilization of water and N from the soil pool to the stream (Bernal *et al.*, 2013). However, rewetting events can also induce pulses of microbial immobilization (Harms & Grimm, 2010; Dijkstra *et al.*, 2012), denitrification (Butturini *et al.*, 2003; Tiemann & Billings, 2012), and biological uptake (Harms & Grimm, 2010; Jongen *et al.*, 2013) if there is enough time for biota and solute media to interact. Thus, the effect of microbial pulses on stream N export will depend on how quickly water is transferred from terrestrial systems to streams (Meixner & Fenn, 2004; Lohse *et al.*, 2013). This idea is well illustrated by Lupon *et al.* (2016a), who simultaneous quantified stream N loads and net nitrification rates in three forest types (oak, beech, and riparian) of a Med catchment under a wide range of antecedent moisture conditions. The study showed a contrasting influence of net nitrification rates on stream NO_3^- loads between Med uplands and riparian soils. As expected for N-limited ecosystems, there was a weak relation between upland nitrification and stream N loads, suggesting that most of the NO_3^- produced in upland soils tended to be retained within the catchment (Fig. 2a and 2b). The capacity of terrestrial ecosystems to retain N was especially noticeable during hot moments, when stream N loads did not increase despite the extremely high nitrification rates observed in the upland soils. Conversely, stream NO_3^- loads were strongly related to nitrification in riparian soils (Fig. 2c), highlighting their potential to enhance catchment N losses due to their proximity and strong hydrological connection with the adjacent aquatic ecosystems. These findings are in agreement with recent modelling approaches, which suggest that riparian soils can be critical for understanding the temporal pattern of N budgets and exports in Med catchments (Medici *et al.*, 2010; Lupon *et al.*, 2015). In particular, model simulations suggest that the influence of riparian soils on N exports may be maxima in summer and early-fall, when warm and well oxygenated soils can enhance nitrification rates and NO_3^- leaching. All together these studies highlight that, despite upland systems have a strong influence on catchment N exports, the role of riparian hydrology and biogeochemistry on modulating stream N exports can be equally important.

RIPARIAN EVAPOTRANSPIRATION AS A DRIVER OF STREAM N EXPORTS

In most Med systems, upland water requirements are high, and thus, riparian ET (450-600 mm yr^{-1}) contributes minimally ($< 5\%$) to the total annual catchment water depletion (Sabater & Bernal, 2011; Lupon *et al.*, 2016b). Nonetheless, riparian ET can strongly influence the temporal pattern of stream hydrology as well as the hydrological connectivity between riparian zones and streams (Fig. 3). On a sub-daily basis, riparian vegetation can induce a variation in stream discharge up to 20% by taking up water from the riparian aquifer or directly from the stream (Lundquist & Cayan, 2002; Lupon *et al.*, 2016b) (Fig. 3b). Moreover, during the vegetative period, riparian ET can contribute to decrease the riparian groundwater elevation and increase stream hydrological retention (i.e. the displacement of water from the stream to the riparian zone) (Rassam *et al.*, 2006; Lupon *et al.*, 2016b) (Fig. 3c). The seasonal influence of riparian ET on catchment hydrology becomes more accentuated in drier climates, where drawbacks in the groundwater table can induce premature abscission of riparian tree leafs (Sabater & Bernal, 2011) and the complete desiccation of the stream channel (Butturini *et al.*, 2003; Medici *et al.*, 2008).

From a catchment perspective, several studies have shown that stream hydrological retention increase from headwaters to the valley bottom (Covino *et al.*, 2010; Montreuil *et al.*, 2010; Bernal & Sabater, 2012). Yet, there are few empirical evidences linking the longitudinal variation of stream hydrology with riparian water requirements. A recent study conducted in the NE of the Iberian Peninsula showed that, during the vegetative period, stream hydrological retention occurred often at the valley bottom of a headwater catchment (60% of time), where a well-developed riparian forest ensured high ET rates compared to headwaters (Fig. 3) (Lupon *et al.*, 2016c). In this line of thought, pioneer modelling approaches indicate that the riparian compartment is crucial for successfully simulate the non-linear behavior of stream hydrology at the valley bottom of Med catchments (Medici *et al.*, 2008; Lupon, 2015). These results contrast with those found in temperate streams, where water exports mostly depend on seasonal changes in precipitation and upland ET (Futter *et al.*, 2014; Kim *et al.*, 2014); and suggest that riparian ET could be critical to predict water and nutrients exports in regions experiencing some water limitation.

Riparian ET can not only influence stream discharge, but also stream N concentrations because the water moving towards the riparian zone

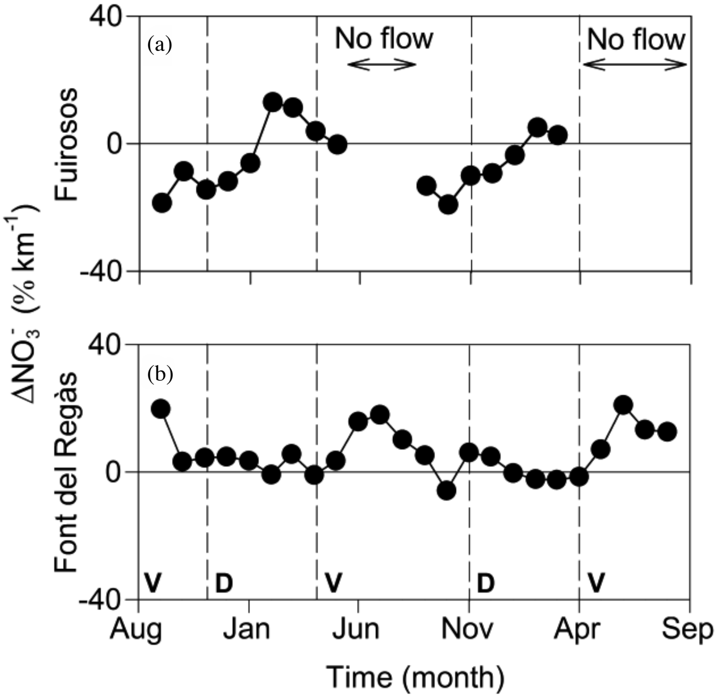

Figure 4. Temporal pattern of the relative difference in monthly volume-weighted stream nitrate concentration (ΔNO_3^-) between the headwaters and the valley bottom of (a) a semi-arid Med catchment (Fuirosos) and (b) a sub-humid Med catchment (Font del Regàs). The two catchments, located < 50 km apart, were mostly forested and received similar amounts of atmospheric N deposition (15 kg N year^{-1}). However, catchments had different annual precipitation (613 mm in Fuirosos vs. 980 mm in Font del Regàs) and hydrologic regime (temporal in Fuirosos vs. permanent in Font del Regás). For each month, $\Delta NO_3^- = (C_{valley} - C_{headwater})/C_{headwater}$ and was expressed by km of reach length. Values of $\Delta NO_3^- > 0$ indicate when stream nitrate concentration increased along the reach, while $\Delta NO_3^- < 0$ indicates the opposite. The figure shows the contrasting behavior of both reaches during the vegetative period; Font del Regàs release nitrate, while Fuirosos uptake nitrate. Adapted from Bernal and Sabater (2012) and Lupon *et al.* (2016b). *Variación temporal de la diferencia relativa en las concentraciones de nitrato (ΔNO_3^-; ponderadas por el volumen) entre la cabecera y el fondo de valle de un tramo de río en (a) una cuenca semi-árida (Fuirosos) y (b) una cuenca sub-húmeda (Font del Regàs). Ambas cuencas, situadas a < 50 km de distancia, eran mayormente forestadas y recibían una cantidad similar de deposición atmosférica (15 kg N año^{-1}). Las cuencas diferían en la precipitación anual (613 mm en Fuirosos vs. 980 mm en Font del Regàs) y en el régimen hidrológico (temporal en Fuirosos vs. permanente en Font del Regàs). Para cada mes, $\Delta NO_3^- = (C_{valley} - C_{headwater})/C_{headwater}$ y es expresada en km de longitud de tramo fluvial. Valores de $\Delta NO_3^- > 0$ indican periodos durante los cuales las concentraciones de nitrato incrementan a lo largo del tramo, mientras que $\Delta NO_3^- < 0$ indica lo contrario. La figura muestra el comportamiento contrastado de ambos ríos durante el período vegetativo; Font del Regàs libera nitrato, mientras que Fuirosos retiene nitrato. Figura adaptada de Bernal and Sabater 2012 y Lupon* et al. *(2016b).*

can enhance the biological N assimilation near the stream-riparian edge and reduce up to 60% the stream DIN concentration (Schade *et al.*, 2002, 2005). Moreover, riparian ET can favor the interaction between the water column and the hyporheic zone because, during periods of hydrological retention, the dominance of subsurface flow increase respect to the surface flow (Dahm *et al.*, 1998). Presumably, hyporheic zones in Med streams are regions of high heterotrophic activity and oxygen poor environments, and therefore, a sharp decrease of stream NO_3^- concentration is expect to occur due to high rates of N uptake and denitrification (Kemp & Dodds, 2002; Brooks & Lemon, 2007; Bernal *et al.*, 2013). However, it has been shown that some arid streams can hold well-oxygenated hyporheic zones even during low discharges periods, which can favor in-stream N mineralization and nitrification, and consequently, increase rather than decrease stream NO_3^- concentrations (Holmes *et al.*, 1994; Jones *et al.*, 1995).

Ultimately, the combination of biogeochemical processes occurring within streams, riparian and hyporheic zones would determine downstream N fluxes. In some Med catchment, a large drop in stream NO_3^- concentrations and fluxes has been observed from headwaters to the valley bottom, likely as a result of the biological N assimilation in the stream-riparian edge, the stream water column, and/or the hyporheic zone (Meixner & Fenn, 2004; von Schiller *et al.*, 2008; Bernal & Sabater, 2012) (Fig. 4a). Conversely, other studies have reported longitudinal increases in stream NO_3^- concentrations when NO_3^- release processes (i.e. nitrification) overwhelm biological N assimilation (Fig. 4b) (Dent *et al.*, 2007; Bernal *et al.*, 2015; Lupon *et al.*, 2016c). The reasons for differences in the N processing along the river continuum remain unclear, though these different patterns likely respond to differences in riparian vegetation, streambed substrate, organic matter availability, redox conditions, and water residence time (Brooks & Lemon, 2007; Abbott *et al.*, 2016). Moreover, the degree of hydrological interactions among the riparian, hyporheic, and stream water compartments may be fundamental to understand the efficiency of riparian biota to mediate stream N fluxes (Abbott *et al.*, 2016). This idea was well illustrated by Dent *et al.* (2007), who showed that the capacity of riparian zones to remove N from an arid stream in Arizona varied strongly (from 7-67%) depending on whether stream water entered uniformly or only at specific locations to the riparian zone. Overall, the abovementioned studies pinpoint that the timing and extent of hydrological connectivity between catchment units is key for improving our ability to predict N retention and exports from catchments (Dent *et al.*, 2007; Pinay *et al.*, 2015; Abbott *et al.*, 2016).

RIPARIAN CANOPY AS A REGULATOR OF IN-STREAM N CYCLING

Riparian canopy can play a fundamental role in controlling seasonal changes in stream metabolism in Med regions because it regulates both light and organic matter inputs to the stream channel (Guasch & Sabater, 1995; von Schiller *et al.*, 2007). However, our understanding of how riparian canopy influences stream N cycling by driving stream metabolism is limited. In a pioneer study, Sabater *et al.* (2000) found that both algae biomass and NH_4^+ uptake rates were higher in an open-canopy than in a riparian shaded stream reach, suggesting that riparian canopy may limit the in-stream capacity to take up N from the water column. More recently, Lupon *et al.* (2016c) showed that gross primary production and associated diel variations in stream NO_3^- concentrations decreased as the riparian crown closed and limited light inputs into the stream (Fig. 5). Interestingly, the study showed no diel NO_3^- variations in riparian groundwater, evidencing that in-stream photoautotrophic activity alone was responsible for the diel cycles in NO_3^- concentration (Fig. 5c). This result is important because allowed separating the influence of riparian vs in-stream processes on stream N dynamics, and further, highlights that stream primary production is directly linked to the phenology of the riparian trees. Moreover, Lupon *et al.* (2016c) nicely illustrated the importance of stream metabolism in regulating catchment

N exports by showing that in-stream photoautotrophic activity reduced by 10% the catchment NO_3^- export in spring. These results are comparable to those reported for high productivity rivers (Grimm, 1987; Heffernan & Cohen, 2010), suggesting that photoautotrophs can substan-

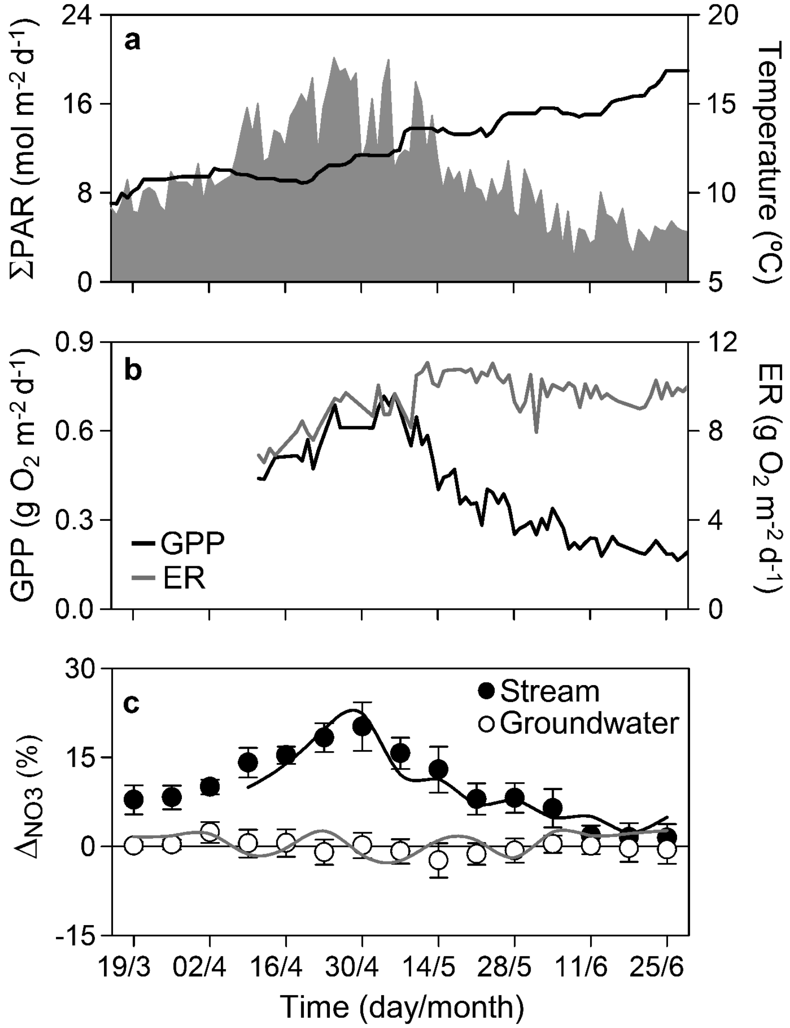

Figure 5. Temporal pattern of (a) environmental conditions, (b) stream metabolism, and (c) diel nitrate variations (expressed as the relative difference between midnight and noon concentrations) during spring at the valley bottom of a Med catchment. Panel (a) shows daily photosynthetically active radiation (ΣPAR) (grey shadow) and mean daily stream water temperature (black line). Panel (b) shows data for gross primary productivity (GPP; black line) and ecosystem respiration (ER; gray line). Panel (c) shows data for stream water (black circles) and riparian groundwater (white circles). Solid lines represent the predicted day-night variations in stream nitrate concentration calculated from GPP rates (black line) and from hydrological mixing with groundwater (grey line). Light inputs to the stream favored in-stream GPP and photoautotrophic N uptake before the riparian canopy closure. Adapted from Lupon *et al.* (2016c). *Variación temporal de (a) los factores ambientales, (b) las tasas metabólicas y (c) la variación diaria de nitrato (expresada como la diferencia relativa entre las concentraciones medidas en la medianoche y el mediodía) durante la primavera en el fondo del valle de una cuenca mediterránea. El panel (a) muestra los valores diarios de radiación solar (ΣPAR) (sombra gris) y temperatura media (línea negra). El panel (b) muestra las tasas de producción primaria bruta (GPP, línea negra) y respiración del ecosistema (ER, línea gris). El panel (c) muestra los valores de ΔNO_3^- en el río (círculos negros) y en el freático de ribera (círculos blancos). Las líneas sólidas representan la variación día-noche calculada a partir de las tasas de GPP (línea negra) y a partir de la mezcla hidrológica con el agua del freático (línea gris). Las entradas de luz favorecen la producción primaria bruta y la asimilación fotoautotrófica de nitrógeno justo antes de cerrarse el dosel ribereño. Figura adaptada de Lupon* et al. *(2016c).*

tially contribute to transitorily reduce catchment N losses even in highly heterotrophic forested streams.

Riparian leaf litter abscission during late-summer and early-fall has also a strong influence on stream hydrology and nutrient biogeochemistry. Large stocks of organic matter increase water transient storage zones and promote the interaction between stream biota and fresh organic matter, which can favor the development of microbial communities and lead to high values of ecosystem respiration, in-stream N mineralization, and stream NH_4^+ concentrations (Acuña *et al.*, 2004; Argerich *et al.*, 2008; Bernal *et al.*, 2012). In some cases, the rapid mineralization of leachates may also increase the N demand of stream biota and favor in-stream NH_4^+ uptake (Argerich *et al.*, 2008; Bernal *et al.*, 2012) and nitrification (Acuña *et al.*, 2005; Bernal *et al.*, 2015; Lupon *et al.*, 2016b). Altogether, the previous studies suggest that Med riparian zones can be important sources of organic N via litterfall, which can be mineralized and nitrified within the stream under favorable conditions. Moreover, the presence of N_2-fixing species such as *Alnus glutinosa* or the invasive *Robinea pseudoacacia* can enhance stream N cycling by providing N-rich leaf litter (Starry *et al.*, 2005; Mineau *et al.*, 2011), and thus, natural or human induced changes in riparian species composition could have a strong impact on stream nutrient dynamics.

CONCLUSIONS AND FINAL REMARKS

Riparian zones can play a key role in regulating the N cycle in Med continental systems, yet understanding their influence on catchment N exports is still limited. In this review, we have shown that fundamental differences exist in the biogeochemistry of Med riparian zones compared to more humid ones that precludes the direct application of existing knowledge from temperate regions. For instance, we showed that riparian soils can be hot spots of N supply within Med catchments because they are N-rich, well oxygenated, and relatively wet. Moreover, Med riparian soils can be potential sources of DIN to the streams due to their proximity and strong hydrological connection with adjacent aquatic ecosystems; which contrast with the N sink behavior typically reported in more humid riparian zones (McClain *et al.*, 2003). Interestingly, the contribution of Med riparian soils to catchment N export is expected to increase in the future because they are highly responsive to warming (Duncan *et al.*, 2015; Lupon *et al.*, 2015). In particular, simulations from a mechanistic model suggest that N mineralization and nitrification rates in Med riparian soils could increase by 6-11% over the next century, which would increase the amount of NO_3^- that can be leach out to fluvial ecosystems (Lupon *et al.*, 2015). Moreover, future change in climate may alter the composition and structure of riparian forests, thus affecting the soil N pool and exports (Medina-Villar *et al.*, 2015; Bruno *et al.*, 2016). Taken together, the previous studies suggest that riparian soils may be essential to understand present and future temporal patterns of N exports in Med catchments and stress the importance to consider this catchment pool as a potential source of other essential nutrients.

The results presented here illustrate that riparian ET can influence catchment N export by mediating both stream discharge and N concentrations. From a hydrological perspective, riparian ET can have a disproportionately large impact on water resources by dropping down riparian groundwater levels, promoting stream hydrological retention, and decreasing stream discharge. Previous studies have shown that relatively small decreases in annual precipitation can markedly increase the relative contribution of riparian ET to catchment water budgets, suggesting that future climate alterations could exacerbate the impact of Med riparian zones on catchment water resources (Lupon *et al.*, 2016b). Therefore, we propose that this catchment pool should be considered to a further extent when modeling stream hydrology, as well as for a sound and integrated management of catchment water resources.

From a biogeochemical point of view, the exchange of water between streams and riparian zones induced by riparian ET can promote the N filter capacity of riparian ecosystems by enhancing biotic N uptake at the stream-riparian edge. However, in-stream processes (either N uptake and/or release) can screen to some extend the influence of riparian processes on stream N dynamics. Indeed, a whole-reach mass balance approach based on monthly samplings revealed that in-stream N processing was at least as important as net riparian groundwater inputs for understanding the longitudinal pattern of stream DIN concentrations (Bernal *et al.*, 2015). Overall, the studies condensed in this review suggest that Med riparian zones may have a limited capacity to decrease catchment N export, and question the well-established idea that riparian zones are efficient N buffers, at least for catchments experiencing some degree of water limitation.

Riparian phenology can also control in-stream N cycling and even catchment N export during some periods. We have shown that canopy leaf-out controls the magnitude of in-stream photoautotrophic activity and the associated N uptake, while leaf litterfall burst ecosystem respiration in summer and fall. Climate change is already influencing riparian tree phenology by promoting an earlier emergence of riparian tree leaves and longer vegetative periods (Perry *et al.*, 2012). These alterations may have implications for N cycling in Med streams because photoautotrophic N uptake can only occur when both light and temperature conditions are favorable (Lupon *et al.*, 2016c). Moreover, future warming and drying conditions may influence the annual distribution of riparian leaves abscission, as the amount of leafs falling in summer is inversely related to precipitation and stream flow in Med streams (Sanpera-Calbet *et al.*, 2016). The premature leaf abscission of riparian trees, together with warmer temperatures, could increase N release processes and dissolved N concentrations in Med streams in late-summer, leading to environmental issues such as downstream eutrophication.

Finally, findings gathered in this review suggest changes in the structural or functional traits of riparian zones can influence in-stream N cycling along the river continuum, thus affecting catchment N exports from headwaters to the valley bottom. We have shown that the influence of riparian ET on stream hydrology as well as the capacity of riparian trees to regulate stream light and leaf litter inputs increase from headwaters to the valley bottom and have a substantial effect on in-stream N cycling. Overall, we have learned about the importance of studying a particular biogeochemical process or ecosystem within a broader context in order to get a more complete picture of their ecological role at relevant spatial and temporal scales. However, and paradoxically, most catchment studies focus mostly on upland ecosystems (Goodale *et al.*, 2009; Ross *et al.*, 2012), while studies assessing in-stream nutrient cycling do not consider the interaction between the stream and riparian groundwater (Heffernan & Cohen, 2010; Bernal *et al.*, 2012). The simplification of empirical approximations is unavoidable and it has been shown to be helpful for understanding some patterns and drivers of complex systems such as forest, riparian, and streams. Yet, the implications of the obtained results are constrained to the scale of observation and difficult to link with processes occurring at larger scales more relevant from an ecosystem perspective. Hence, we suggest that future catchment research should take into account, as much as possible, the links between upland, riparian, and in-stream biogeochemical cycles to be able to quantify their potential role as regulators of water, nutrients, sediments, and pollutants within landscapes. This is a true challenge for both forest and stream ecologists and, at the same time, an essential exercise in order to advance catchment biogeochemistry and develop integrated management strategies that successfully mitigate future increments in anthropogenic N inputs.

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