Universidad de Concepción

Facultad de Ciencias Ambientales
Programa de Doctorado en Ciencias Ambientales mención Sistemas Acuáticas Continentales

Influencia hidrológica sobre la biogeoquímica fluvial en un río intermitente del Mediterráneo Chileno

Tesis para optar al grado de

Doctora en Ciencias Ambientales con mención en Sistemas Acuáticos Continentales

Katherine Charlene Brintrup Barría

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"*Cuando trates con el agua consulta primero la práctica, y luego la teoría*"

Leonardo da Vinci

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Agradecida de la vida
por darme hermosos hijos
Vicente y Dominga

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RESUMEN

Los ríos intermitentes y arroyos efímeros (IRES) son sistemas fluviales altamente dinámicos, sujetos a periodos de sequía, esporádicos caudales y en ocasiones grandes avenidas. Son considerados reactores biogeoquímicos puntuales, con alta capacidad de resiliencia ante periodos de sequía y posterior reconexión.

Por lo tanto, se plantea que en la fase de fragmentación de los IRES se acumulará gran cantidad de materia orgánica de alto potencial productivo, y la posterior reconexión del flujo implicaría un incremento en la concentración de nutrientes en el agua superficial y disminución en el agua de hiporreo, así como se cree que habrán elevadas tasas de emisión de CO_2 atmosférico. Posteriormente, en eventos de lluvia, el caudal podría ser predictor de la dinámica biogeoquímica del agua superficial.

En relación a lo anterior, el objetivo del estudio fue cuantificar y comparar la dinámica de las variables biogeoquímicas, tales como materia orgánica particulada gruesa, nutrientes, sólidos, carbono orgánico disuelto (DOC) y propiedades de la materia orgánica disuelta (DOM), en las fases de contracción, fragmentación, rehumectación y expansión de un río intermitente de Chile Mediterráneo, con otros IRES y perennes. Para cumplir con el objetivo planteado, se seleccionaron ríos intermitentes y perennes del mediterráneo Chileno de la Región del Ñuble, así como de otros climas en diversas regiones del mundo. Durante la fase seca se tomaron muestras de materia orgánica, sedimento y biofilm en los lechos de los ríos, se cuantificó este material, se estimó su potencial productivo y mediante ensayos en laboratorio se calculó la emisión de CO_2 atmosférico luego de un primer pulso de inundación. En la misma fase, también se tomaron muestras de agua superficial y de hiporreo en las pozas de ríos intermitentes, para analizar nitrógeno inorgánico disuelto (DIN), nitrógeno total (TN), fósforo total (TP), sólidos suspendidos y disueltos (DS y SS) y DOC, posteriormente se repite esta metodología en la reconexión durante dos años consecutivos, para comparar los cambios biogeoquímicos impulsados por la reconexión. Finalmente, se realizan muestreos continuos en tres eventos de lluvia para analizar DIN, TN, TP, DS, SS, DOC, propiedades de DOM y así determinar el transporte total y origen de solutos, propiedades de DOM y establecer relaciones entre el caudal y las variables.

Los resultados indican que los IRES estudiados no obedecen a patrones en los distintos periodos y sitios. Pese a que la vegetación ripariana es similar en ríos perennes e intermitentes, los IRES de Chile Mediterráneo pueden acumular gran cantidad de materia orgánica, de alto potencial productivo en comparación con los perennes, en promedio 1 029 g m^{-2} en IRES y 337 g m^{-2} en perennes equivalente a 6.86 y 2.46 g m^{-2} d^{-1}, respectivamente. La cantidad y calidad de materia orgánica que se acumula en los lechos de los ríos intermitentes muestreados influye sobre el CO_2 que ellos emiten en un pulso de inundación, generando 539.37 mg. CO_2 m^{-2} d^{-1}, similar al promedio global (883.19 mg. CO_2 m^{-2} d^{-1}).

En las pozas que permanecen durante la fase seca no se encontró un patrón en las variables entre fragmentación y reconexión en el agua superficial y de hiporreo, así como tampoco se observan condiciones de anoxia. Se presume que los nutrientes pueden ser procesados rápidamente por las bacterias del hiporreo en el primer pulso de inundación.

En episodios de lluvia no se observó un patrón en el origen de los solutos, a excepción de DIN, que proviene siempre desde el lecho y agua subterránea. Se observa en todos los casos que un incremento del caudal implica que la calidad de la DOM sea predominantemente aromática, más liviana, de mayor tamaño, menos autóctona, y los resultados de modelación indican que el caudal puede ser un predictor útil del comportamiento de los solutos estudiados. Por lo tanto cada fase hidrológica tiene características únicas que puede estar asociada a la época del año, el tipo de soluto, humedad del suelo o intensidad de la tormenta.

Dado el incremento de IRES y la vulnerabilidad que presentan los sistemas acuáticos en Chile frente al cambio climático, se da énfasis en la necesidad de continuar esta línea de investigación en otras regiones del país, para generar una base de datos robusta y de esa forma generar estrategias de protección en IRES.

INTRODUCCIÓN GENERAL

Los ríos intermitentes y arroyos efímeros (IRES) son sistemas fluviales altamente dinámicos, cuyo flujo cesa en algún punto o momento del año (Larned et al., 2010; Acuña et al., 2014; Datry et al., 2018a). Mantienen un ciclo hidrológico anual con fases de contracción, fragmentación, desecación y reconexión del flujo (Froebrich 2005; Lillebo et al., 2007; von Schiller et al., 2011), donde los eventos de sequía y rehumedecimiento forman ecosistemas en transición entre la fase terrestre y acuática (Datry et al., 2014; 2018a), que determinan las tasas de procesamiento de nutrientes y distribución espacial de organismos que participan en el proceso (Dent y Grimm 1999).

Los IRES constituyen una proporción sustancial del número total de ríos del mundo, estimada en más del 50% de la red global (Larned et al., 2010; Shumilova et al., 2019), por lo tanto, drenan gran proporción de superficie terrestre en todos los continentes y distintos tipos de clima (Stanley et al., 1997; Acuña et al., 2014; Datry et al., 2016; Datry et al., 2018b). En Estados Unidos hay al menos 3 200 000 km de IRES, que equivalen al 60% de la longitud total de los ríos en dicho país (Nadeau y Rains 2007) y el 43% de la superficie de Grecia está drenado por IRES (Tzoraki y Nikolaidis 2007). En Italia, el 50% de la red de 2700 km del río Tagliamento es intermitente (Doering et al., 2007). Se pronostica que en el siguiente siglo el número y longitud de IRES incrementará en regiones que muestran tendencia a la sequía debido por una parte al cambio climático, y por otra, a la presiones antropogénicas que alteran los regímenes hídricos, tales como desvío de agua, extracción de agua para fines socio-económicos y alteración del uso de suelo, promoviendo la prevalencia de la intermitencia del flujo, tanto espacial como temporalmente (Larned et al., 2010; Pekel et al., 2016; Datry et al., 2017; Shumilova et al., 2019). Actualmente se observan tendencias a la disminución de caudales en ríos de diversas regiones del mundo (Zhang et al., 2001; Pasquini y Depetris 2006; Tockner et al., 2009). En el suroeste de Australia, los flujos en las últimas décadas han disminuido en más del 50% luego de una caída del 16% en las precipitaciones (Silberstein et al., 2012) y con el uso de modelos se ha propuesto una disminución de la escorrentía en regiones de latitudes medias (Huntington 2006; Kundzewicz et al., 2008).

Chile es uno de los 10 países más vulnerables al cambio climático (IPCC 2014), además se estima una disminución en las precipitaciones de un 30-15% en la zona central-sur (Quintana y Aceituno, 2012), esto afectará el caudal de ríos perennes, incrementará la cantidad de ríos intermitentes y sus periodos de sequía, que serán más intensas en la región mediterránea de Chile, dado que aquí se concentra la mayor población humana y por lo tanto, las mayores presiones sobre el sistema hídrico.

Los ríos y arroyos, en general transportan gran cantidad de componentes en forma particulada y disuelta (Meybeck 1982), tales como materia orgánica (MO) y nutrientes, que son fuente principal de energía y carbono (C), fundamentales para el funcionamiento de todo ecosistema (Howarth et al., 1996). La MO y nutrientes son aportados principalmente desde la cuenca (fuentes alóctonas), y al ingresar al río comienzan los procesos de descomposición (Tank et al., 2010). Los nutrientes más importantes son el nitrógeno (N) y fósforo (P), porque pueden limitar la productividad en ecosistemas acuáticos, aunque en exceso generan eutrofización de los cuerpos de agua (Conley et al., 2009). La dinámica de MO y nutrientes dentro del río puede incluir el ingreso, salida, procesamiento o remoción de estos componentes, determinando el estado trófico del sistema, así como su estructura y funcionamiento (Molholland y Webster 2010). Esta dinámica ha sido extensamente estudiada en ríos y arroyos perennes (Molholland y Webster 2010; Tank et al., 2010), pero en IRES este conocimiento es menor (Bernal et al., 2013; Datry et al., 2014; von Schiller et al., 2017). Durante algunos periodos, ambos tipos de ríos son similares, dado que los factores que controlan la dinámica de MO y nutrientes ocurren en condiciones hidrológicas aparentemente iguales, sin embargo, no comparables, dado que los IRES tienen intermitencia de su flujo con épocas alternadas de sequía y rehumedecimiento, con una consecuente variabilidad lateral, vertical y longitudinal (von Schiller et al., 2017). También existen diversos subsistemas que se forman en el lecho de estos ríos en época de sequía, así como entre el río y la vegetación ribereña. Esta heterogeneidad espacial y temporal determina la dinámica de la MO y los nutrientes en IRES (Bernal et al., 2013; von Schiller et al., 2017).

Generalmente los IRES presentan 4 fases hidrológicas, la primera comienza con la reducción de la precipitación, lo que resulta en una notable reducción del flujo superficial del río, generándose la llamada *contracción* del sistema. A continuación, el aumento de la temperatura y evaporación del agua superficial provocan la *fragmentación*, aquí cesa el flujo superficial del río y en algunos casos se forman pozas aisladas, cuando estas desaparecen totalmente, ocurre la desecación superficial. Por último, con el retorno de las precipitaciones y disminución de la temperatura, el flujo del río se reconecta, con el primer pulso de inundación en la fase llamada *rehumectación*, las siguientes precipitaciones de la temporada propician la *expansión* del río (Figura 1). Estas 4 fases ocurren con mayor frecuencia en regiones de clima mediterráneo, árido y semiárido (Larned et al., 2010; von Schiller et al., 2017).

Debido a su hidrología altamente dinámica, los IRES son considerados reactores biogeoquímicos puntuales, presentando variaciones espacio-temporales de ingreso de materia orgánica y nutrientes, cuyo almacenamiento, procesamiento y transporte está determinado por las fluctuaciones de cese de flujo y rehumectación (Larned et al., 2010; Datry et al., 2014; von Schiller et al., 2017). Estos patrones biogeoquímicos pueden diferir entre ríos, durante las fases de *contracción*, *fragmentación, rehumectación* y *expansión*, según el clima, latitud, régimen hídrico, tiempo de senescencia y presencia de vegetación ribereña (Boyero et al., 2017; Datry et al., 2018b; Shumilova et al., 2019; Tiegs et al., 2019). Además de las variaciones biogeoquímicas durante estas fases, existe una dinámica espacial de nutrientes y MO, debido a una alta interacción hidrológica entre el agua superficial y de hiporreo, tanto en la zona ripariana como parafluvial, dado que IRES son sistemas terrestres-acuáticos (Jones y Molholland 2000).

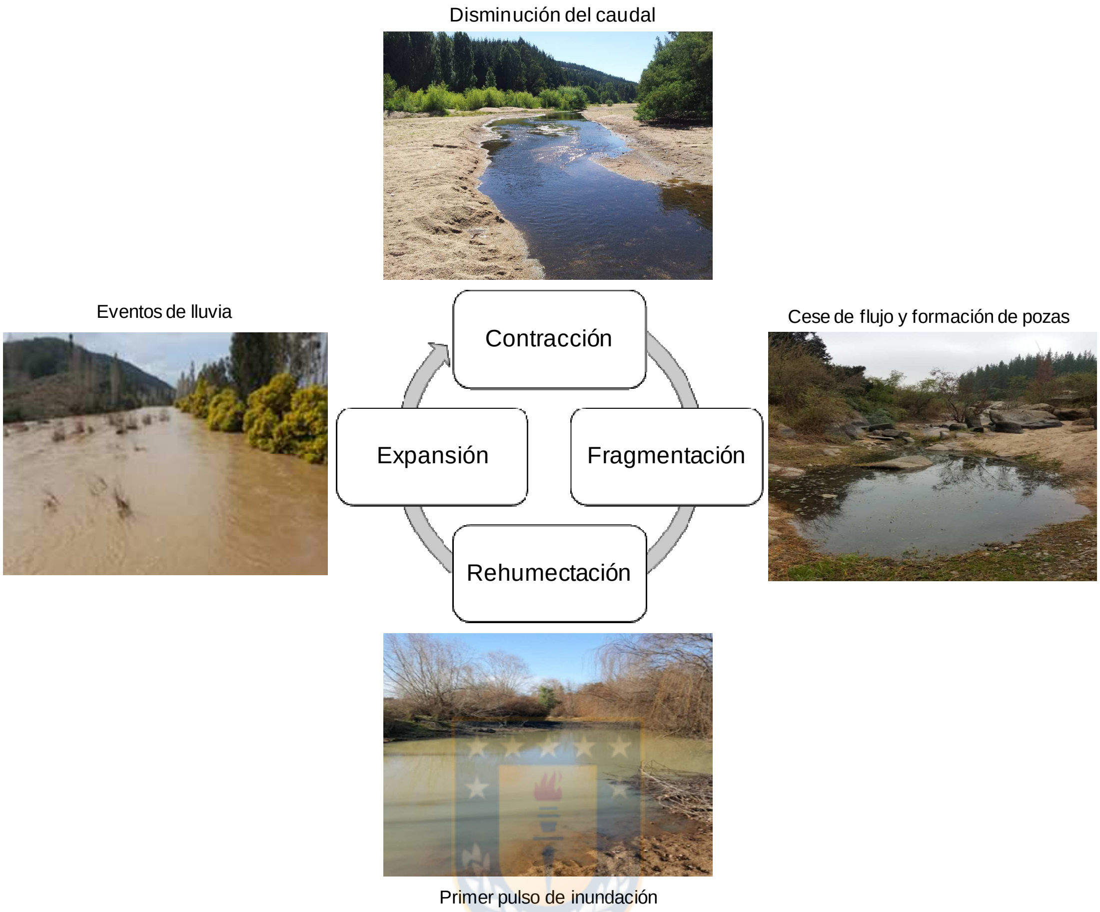

Figura 1. Fases hidrológicas en ríos intermitentes y arroyos efímeros. Imágenes del río intermitente Lonquén, XVI Región del Ñuble, Chile.

En los IRES, el procesamiento de nutrientes depende de las fases ya descritas que favorecen la dinámica temporal y espacial de nutrientes (Boulton y Lake 1990; Stanley et al., 1997; Dent y Grimm, 1999; Baldwin et al., 2005; Arce et al., 2013). Por ejemplo, durante la sequía, la mortalidad microbiana y la exposición prolongada del sedimento libera gran cantidad de nitrógeno y fósforo (Baldwin y Mitchell 2000; Amalfitano et al., 2008). Por otro lado, la expansión del flujo con los eventos de lluvia, están asociados al incremento de nutrientes y materia orgánica disuelta (DOM), lo cual eleva las tasas de productividad fotosintética y bacterias heterótrofas, ocasionando cambios en las cadenas tróficas (Wetzel 1992; Buffam et al., 2001; Peterson et al., 2001; Ensign y Doyle 2006). Estos procesos biogeoquímicos podrían ser aún más dinámicos en IRES porque están adaptados a las condiciones hidrológicas extremas (Larned et al., 2010; Datry et al., 2014). Los estudios de Scherer et al. (1984), Vincent y Howard-Williams (1986), Austin et al. (2004) y Sponseller (2007) indican que se requiere una inundación de pocos minutos para que se activen las bacterias nitrificantes, desnitrificantes, la hitratación en larvas anhidrobióticas de quironómidos y la fotosíntesis en alfombras de cyanobacterias (Larned et al., 2010).

Muchos de estos procesos biogeoquímicos ocurren en la zona hiporreica (HZ), esta es un ecotono activo y se encuentra entre el agua superficial y subterránea de pozas aisladas o sectores más húmedos. Aquí ocurren procesos biogeoquímicos (Mulholland et al., 2000; Puckett et al., 2008; Krause et al., 2009), donde la hidrología, tiempo de residencia, humedad, entre otros factores, influyen sobre la absorción del carbono orgánico disuelto y la nitrificación, definida como la transformación biológica de formas reducidas de nitrógeno a nitrato (Boulton et al., 1998; Koops y Pommerening-Röser 2001). Por otro lado, el agua superficial aporta oxígeno y compuestos orgánicos a los microorganismos e invertebrados de la HZ, mientras que la subterránea suministra nutrientes a los organismos de la columna de agua (Boulton et al., 1998). De modo que la HZ puede influir en la disminución de los niveles de nitrato (NO_3^-) en el agua superficial debido a los procesos de desnitrificación, ya que el NO_3^- es reducido por microorganismos en condiciones anóxicas (Puckett et al., 2008; Krause et al., 2009). Por esta dinámica ampliamente estudiada (Boulton et al., 1998; Mulholland et al., 2000; Peterson et al., 2001; Puckett et al., 2008; Krause et al., 2009; Arce et al., 2013), se reconoce como una zona donde existen mecanismos de atenuación de nutrientes (Smith 2005; Environment Agency 2000), otorgándole una valoración intrínseca, más aún cuando en los IRES se acentúa el procesamiento de nutrientes por la adaptación que tiene la biota microbiana a la intermitencia del flujo (Scherer et al. 1984; Vincent y Howard-Williams 1986; Austin et al., 2004; Sponseller 2007).

En presencia de flujo, los IRES reciben, transportan y procesan la MO originada en la cuenca de drenaje del mismo modo que los ríos perennes, así como también generan servicios ecosistémicos idénticos a los que brindan los ríos perennes, sin embargo, durante la desecación, disminuye la calidad del agua contenida en las pozas, afectando algunos servicios de aprovisionamiento asociados al agua superficial, pero manteniéndose los del agua subterránea, que son menos reconocidos y alterando la mayoría de los servicios ecosistémicos restantes (Datry et al., 2018a).

La transformación de la materia orgánica particulada gruesa (CPOM) en partículas de menor tamaño y materia orgánica disuelta es fundamental para sostener toda forma de vida en los sistemas acuáticos continentales (Gessner et al., 1999), y se considera uno de los procesos ecosistémicos más importantes en la biosfera (Hasler et al., 2016). El material vegetal terrestre alóctono es la fuente de energía y materia fundamental en los ríos y arroyos, su descomposición por medio de microbios y macroinvertebrados detritívoros libera energía y nutrientes que sostienen las cadenas tróficas y son un proceso clave en el ciclo del carbono a escala local, regional y global (Battin et al., 2009; Boyero et al., 2011; Raymond et al., 2013). Pese a esto, los IRES no han sido considerados en el balance global de carbono de los sistemas acuáticos continentales y otros procesos (Datry et al., 2014; 2016; 2018b). Esta exclusión podría ser un grave error, debido a que son importantes reactores biogeoquímicos (Larned et al. 2010; Datry et al. 2014) y, recientemente se ha demostrado que pueden almacenar grandes cantidades de materia orgánica durante la fase seca (Corti et al., 2011; Foulquier et al., 2015).

En esta fase, se favorece la acumulación de CPOM en el cauce (figura 2), la que está relacionada con la morfología del río, características del sustrato del lecho, propiedades físicas de la materia orgánica y la hidrología (Maamri et al., 1994; Hoover et al., 2006; Richardson et al., 2009; Corti et al., 2011). En este sentido, los flujos superficiales y subterráneos influyen sobre el tipo y abundancia de la flora, por ejemplo, a medida que el nivel freático disminuye, incrementa la cobertura de matorrales y disminuye la de bosques, afectando la producción de hojarasca y concentración de nitrógeno inorgánico en el suelo (Lite y Stromberg 2005; Shah y Dahm 2008). El ingreso de CPOM también depende de la estructura, composición y fenología del bosque. Por ejemplo, en bosques de *Eucaliptus* se reduce el ingreso de diversidad y calidad del material vegetal, así como los aportes de nutrientes en comparación con el bosque caducifolio mixto (Molinero et al., 1996; Pozo et al., 1997; Bunn 1998). Factores abióticos también pueden influir en la cantidad y calidad de las hojas depositadas, tales como la precipitación o sequías de verano (Benfield 1997; Marchin et al., 2010; Sanpera-Calbet et al., 2015), e incluso se ha comprobado que la latitud es un predictor importante de calidad de la hojarasca, ya que ésta aumenta con la latitud, y disminuye hacia el ecuador (Boyero et al., 2017).

Figura 2. Materia orgánica particulada gruesa acumulada en lechos de ríos intermitentes de la XVI región del Ñuble, Chile. Esteros; (a) Caña Dulce, (b) Lonquén, (c) Virquinco y (d) Cocinero.

Una vez que ingresa la materia orgánica a los lechos de los ríos secos, se transforma química y físicamente (Gessner et al., 1999). Este proceso de descomposición es mediado por el clima e incrementa bajo condiciones húmedas y cálidas (Aerts 1997; Salinas et al., 2011), en periodos de heladas otoñales, porque se propicia la descomposición e incrementa la calidad de la materia orgánica en plantas ricas en nutrientes (Keskitalo et al., 2005; Cornwell et al., 2008; Marchin et al., 2010). Las defensas físicas y químicas de las hojas, tales como ceras y polifenoles pueden permanecer activas por largo tiempo impidiendo la descomposición (Stout 1989; Coq et al., 2010), lo que afecta el ciclo de nutrientes y la productividad del sistema (Graça et al., 2015). En el caso de lechos de ríos extremadamente secos en época estival, disminuye la actividad microbiana, la lixiviación de la materia orgánica y se interrumpe la colonización de macroinvertebrados acuáticos, favoreciendo la fotodegradación, dado el aumento de la exposición a la acción de la radiación ultravioleta, y el incremento de consumidores terrestres (Austin y Vivanco 2006; Corti y Datry 2012). Parte del material vegetal que es depositado o crece en el lecho del río permanece en las pozas que eventualmente perduran en fragmentación (Stanley et al., 1997). Generalmente el agua superficial de las pozas tiene bajo nivel de oxígeno y elevada temperatura, favoreciendo procesos anaeróbicos como la amonificación (Lillebo et al., 2007; von Schiller et al., 2011; Katipoglu et al., 2012), incrementándose las concentraciones de amonio y otras formas reducidas de nutrientes inorgánicos, en los primeros centímetros del sedimento (Vidal-Abarca et al., 2000; Acuña et al., 2005; Lillebo et al., 2007). El fósforo también puede incrementar en condiciones anaeróbicas, debido a su liberación desde el sedimento a la columna de agua, por su desorpción desde minerales que se reducen en un ambiente anóxico (Baldwin et al., 2000; Lillebo et al., 2007).

Tras la rehumectación termina la sequía y se conecta el flujo superficial, liberándose una serie de compuestos disueltos generados a partir de la lixiviación de las hojas (Nykvist 1963; Gessner 1991; Shumilova et al., 2019). La cantidad de sustancias lixiviadas y sus características físico-químicas, depende de variables ambientales que actúan tanto a escala regional (influenciada por el clima) como local, por ejemplo, la geomorfología del río, el uso del suelo y la cubierta del dosel ribereño (Aerts 1997; Catalan et al., 2013; von Schiller et al., 2017; Datry et al., 2018; Shumilova et al., 2019). Estos solutos lixiviados son fuente esencial de carbono y nutrientes para los organismos heterótrofos que se encuentran aguas abajo (Larned et al., 2010; Rosado et al., 2015), aquí, el exceso de material podría causar efectos adversos, por ejemplo; estrés en la biota acuática o eutroficación e hipoxia, lo que genera en ocasiones la mortalidad de peces, macroinvertebrados y otros organismos acuáticos (Bunn et al., 2006; Hladyz et al. al. 2011).

El primer pulso de inundación puede provocar perturbaciones intermedias poco conocidas (Dayton 1971; Connell 1978; Prat et al., 1986; Flecker y Feifareck´s 1994), con efectos que podrían ser catastróficos y que requieren de mecanismos restauradores (Tzoraki et al., 2007; Obermann et al., 2009; Creed et al., 2017). Estas perturbaciones causadas por la variación del flujo son más relevantes en ríos mediterráneos y son claves en la regulación de las variables bióticas (Gasith y Resh 1999). El lixiviado de CPOM es rico en carbono orgánico disuelto (DOC), y se ha observado que puede contener el 40% del contenido en masa de la hoja, incluyendo azúcares solubles, carbónicos y aminoácidos, sustancias fenólicas, proteínas y nutrientes inorgánicos como fósforo, nitrógeno y potasio (Nykvist 1963; Gessner 1991; Bärlocher 2005; Tzoraki et al., 2007; Ostojic et al., 2013; Arce et al., 2014; Harris et al., 2016; Merbt et al., 2016). Además, los cauces de los ríos pueden cubrirse de biopelículas, compuestas de microorganismos (algas, bacterias y hongos) incrustados en una matriz de sustancias poliméricas extracelulares (Sabater et al., 2016), cuyos remanentes se pueden ver incluso durante la fase seca. El lixiviado de este biofilm puede contener carbono orgánico y nitrógeno altamente biodisponibles, debido a la acumulación de exudados y productos de lisis celular (Schimel et al., 2007; Romaní et al., 2017). La rehumectación y expansión del sistema acuático trae como consecuencia altos niveles de fósforo (P), nitrógeno (N) y sólidos suspendidos, provenientes del flujo subterráneo y procesamiento de materia orgánica acumulada en el lecho del río, que ocurre con los primeros pulsos de inundación (Tzoraki et al., 2007; Obermann et al., 2009; Shumilova et al., 2019). Mientras es transportado, el P puede sufrir captación/liberación, adsorción/desorción, precipitación/disolución o advección/difusión (Vannote et al., 1980; Bryce et al., 1999; Withers y Jarvie 2008; Steward et al., 2012).

Durante la expansión de IRES, tanto DOM como los nutrientes son exportados desde los arroyos y sus cuencas de drenaje hacia ríos de mayor orden y zonas costeras, donde la calidad de éstos regula el metabolismo de los sistemas acuáticos (Meybeck 1982, 1993; Glibert et al., 2001; Cole et al., 2007; Paerl 2009). Los sólidos suspendidos (SS) y disueltos (DS) pueden transportar nutrientes como fósforo y nitrógeno, pero además residuos de pesticidas, trazas de metales pesados, entre otras sustancias; incrementando las tasas de sedimentación en el lecho del río y provocando degradación y/o alteración del hábitat acuático (Valero-Garcés et al., 1999; Oeurng et al., 2011; Cerro et al., 2013; Ramos et al., 2015), como procesos de eutroficación e hipoxia en reservorios, lagos o sistemas costeros (Datry et al., 2014). Por ello, es importante definir las variaciones en los aportes en términos estacionales y la magnitud de los eventos de lluvia, donde la hidrología y las condiciones climáticas precedentes son claves en la dinámica de DOM, nutrientes y sólidos (House y Warwick 1998; Rovira y Batalla 2006; Butturini et al., 2008; Du et al., 2014; Fasching et al., 2016; Guarch-Ribot y Butturini 2016).

En ese sentido, el aumento de caudal asociado a un evento de tormenta, tiene la capacidad de transportar grandes cantidades de nutrientes, materia orgánica, SS y SD (Bowes et al., 2009; Oeurng et al., 2011; Gao et al., 2012; Roach 2013; Raymond et al., 2016; Lloyd et al., 2016), pudiendo alcanzar hasta el 75 % de la exportación anual de nitrógeno (Bernal et al., 2005), siendo predominante la exportación de nitrato aguas abajo (Oeurng et al., 2010). Por lo tanto, la mayor parte del transporte de solutos se presenta con los eventos de lluvia (Figura 3), y la variación de las concentraciones de DOC, nutrientes y sólidos, a menudo están altamente relacionados con el caudal (Ward et al., 2012; Cerro et al, 2013; Du et al., 2014; Guarch-Rivot y Fasching et al., 2015; Ramos et al., 2015; Bowes et al., 2015; Edokpa et al., 2015; Lloyd et al., 2016), aunque se ha demostrado que el incremento en el transporte de nitrógeno inorgánico disuelto (DIN) no necesariamente se asocia a un alza de caudal, porque su origen es principalmente autóctono (Oeurng et al., 2010; Cerro et al, 2013; Du et al., 2014; Ramos et al, 2015).

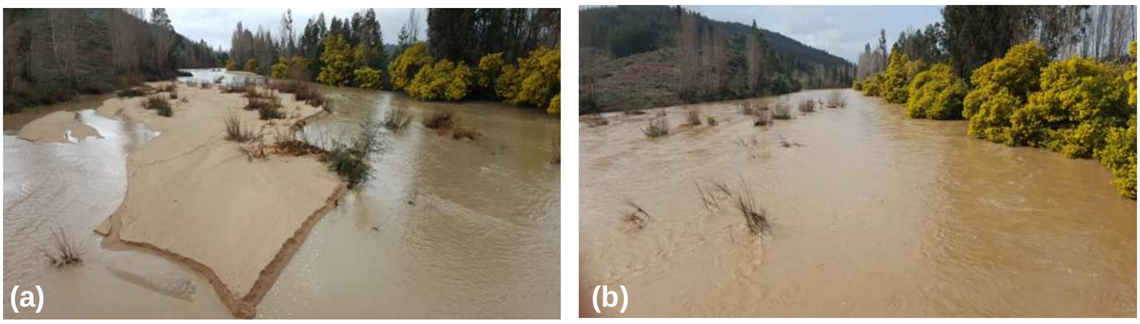

Figura 3. Evento de lluvia en río intermitente Lonquén, XVI Región del Ñuble, Chile. (a) Inicio del evento y (b) 24 horas más tarde.

La calidad de DOM se encuentra bien estudiada mediante espectroscopía (fluorescencia y absorbancia), permitiendo describir su origen alóctono o autóctono

(Parlanti et al., 2000; McKnight et al., 2001; Huguet et al., 2009; Wilson y Xenopoulos 2009), grado de humificación (Chen et al., 1977; Zsolnay et al., 1999), aromaticidad (Weishaar et al., 2003), peso y tamaño molecular (De Haan y De Boer 1987; Helms et al., 2008), entre otras características (Chen et al., 2003; McDonald et al., 2004), que también han sido asociadas al caudal, por ejemplo DOM aromática posee un mayor peso molecular, asociado a caudales elevados (Duan et al., 2007; Fellman et al., 2009; Pellerin et al., 2012; Fasching et al, 2016; Guarch-Rivot y Butturini 2016; Raymond et al, 2016).

Pese a la importancia biogeoquímica de los ríos intermitentes, y la tendencia a su incremento en longitud y cantidad, debido al cambio climático, presiones antropogénicas y limitada protección, existe escasa investigación sobre la dinámica biogeoquímica en las distintas fases de contracción, fragmentación, rehumectación y expansión (Datry et al., 2018b; Shumilova et al., 2019), en especial en IRES de climas mediterráneos (Butturini et al., 2008; Ramos et al., 2015; Guarch-Rivot y Butturini 2016). Por lo tanto, es necesaria una mayor comprensión de la dinámica de MO y nutrientes en las distintas fases hidrológicas de los IRES, en el agua superficial como en hiporreo, mediante estudios *in situ* puntuales de larga data, preferentemente en microcuencas, ya que investigaciones a gran escala pueden no considerar la alta dinámica espacial y temporal que presentan los IRES (Acuña y Tockner 2010; Datry et al., 2014; von Schiller 2014; von Schiller et al., 2017). Estos estudios servirán de base para gestionar su protección en Chile.

HIPÓTESIS DE TRABAJO

H1: Durante las fases de contracción y fragmentación se acumulará mayor cantidad de materia orgánica de alto potencial productivo en comparación a los ríos perennes.
H2: La posterior rehumectación implicará un incremento en la concentración de nutrientes en el agua superficial, disminución en agua de hiporreo y elevadas tasas de emisión de CO_2 atmosférico.
H3: En eventos de lluvia, el caudal puede ser usado como predictor de SS, DS, DOC y características de DOM.

OBJETIVOS

Objetivo general

Cuantificar y comparar la variación de la biogeoquímica (materia orgánica particulada gruesa, nutrientes, sólidos, carbono orgánico disuelto, propiedades de DOM y emisión de CO_2) en las fases de contracción, fragmentación, rehumectación y expansión de ríos intermitentes.

Objetivos específicos

Objetivo 1

Cuantificar y determinar el tipo de materia orgánica particulada gruesa que se acumula durante la fase de contracción y fragmentación en ríos intermitentes y perennes de Chile Mediterráneo.

> Capítulo I: Brintrup K., Amigo C., Fernández J., Hernández A., Pérez F., Félez-Bernal J., Butturini A., Saez-Carrillo K., Yevenes M.A., Figueroa R. (2019). Comparison of organic matter in intermittent and perennial rivers of Mediterranean Chile with the support of citizen science. *Revista Chilena de Historia Natural*. 92(3): 1-10. Doi: 10.1186/s40693-019-0083-3.

Objetivo 2

Determinar los predictores que influyen sobre la acumulación y descomposición de la materia orgánica en lechos de ríos intermitentes en la fase de fragmentación y calcular la tasa de emisión de CO_2 atmosférico a nivel global asociado al primer pulso de rehumectación.

> Capítulo II: Datry T., Foulquier A., Corti R., von Schiller D., Tockner K., Mendoza-Lera C., et al. (2018b). A global analysis of terrestrial plant litter dynamics in non-perennial waterways. *Nature Geosciencie*. 11: 497-503. Doi: 10.1038/s41561-018-0134-4.

Objetivo 3

Evaluar la dinámica de nutrientes en agua superficial e hiporreo en la fase fragmentación y rehumectación de flujo durante dos años hidrológicos consecutivos en un río intermitente de Chile Mediterráneo.

Capítulo III: Brintrup K., Pedreros P., Butturini A., Sáez K., Yevenes M.A., Figueroa R. Dinámica de nutrientes en agua superficial e hyporheo durante la rehumectación de un río intermitente de Chile Mediterráneo.

Objetivo 4

Relacionar la influencia del caudal en la fase de expansión sobre la dinámica de nutrientes, sólidos, propiedades de DOM y su exportación, en un río intermitente de Chile Mediterráneo.

Capítulo IV: Brintrup K., Butturini A., Sáez K., Yevenes M.A., Figueroa R. (Submitted). Biogeochemical dynamics during storm events in an intermittent mediterranean river in Chile. *Environmental Management.*

CAPÍTULO I: Comparison of organic matter in intermittent and perennial rivers of Mediterranean Chile with the support of citizen science

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Abstract
Background: Although intermittent rivers account for over half of the global fluvial network and could increase in length and quantity in Mediterranean climates (in response to climate changes), there is little documentation of organic matter input to them. This study was made possible by the cooperation of the Concepción Chiguayante School community and the Explora project (Chile), with the support of citizen science. The aim was to compare coarse particulate organic matter quantities and types in the Lonquén basin.
Methods: Samplings were performed in two perennial rivers and two intermittent rivers. First, the riparian vegetation of the streams was characterized through photointerpretation and subsequently the organic matter accumulated in the selected river beds was quantified and typified. Spearman's correlation was used.
Results: The riparian vegetation was similar in both types of rivers, though significantly greater ($p<0.05$) plant material accumulation was found in intermittent rivers compared to perennial rivers (1,029 and 337 g m^{-2}, respectively). Likewise, there was a significant relationship among leaves, smaller organic matter, seeds, herbs and shrubs in intermittent rivers.
Conclusions: The results reveal the importance of the intermittent rivers that were sampled as transitory reservoirs of organic matter with high productive potential, especially in the first flood pulses, when this material is transported downstream.
Keywords: Intermittent rivers, citizen science, coarse particulate organic matter, Mediterranean climate.

Introduction

The transformation of coarse particulate organic matter (CPOM) into smaller particles and dissolved organic matter is fundamental to sustain all life forms in continental aquatic systems (Gessner et al., 1999) and is considered one of the most important ecosystem processes in the biosphere (Hasler et al., 2016). Allochthonous terrestrial plant material is the fundamental source of energy and organic matter in both rivers and streams (Vannote et al., 1980). Its decomposition by means of detritivorous macroinvertebrates and microbes (Naiman & Décamps 1997; Raymond et al., 2013) releases energy and nutrients, which in turn support the food web, and is a key process in the local, regional and even global carbon cycle (Battin et al., 2009; Boyero et al., 2011).

Intermittent rivers and ephemeral streams (IRES) have not been considered in the global carbon balance of continental aquatic systems and other biogeochemical processes (Datry et al., 2014; 2016; 2018). This exclusion could be a serious failure due to the fact that they are important biogeochemical reactors (Larned et al., 2010; Datry et al., 2014) and because recently it has been shown that they can store large amounts of organic matter during dry seasons (Corti et al., 2011; Foulquier et al., 2015; Datry et al., 2018). In addition, IRES account for more than half of the global fluvial network (Larned et al., 2010; Acuña et al., 2014). For example, they account for 59% of the total length of the rivers in the United States of America (Nadeau & Rains 2007) and it has been observed that due to anthropogenic pressures such as water extraction, land-use changes and global climate change phenomena (Gleick 2003; Acuña et al., 2014; Jaeger et al., 2014), the flows of many perennial rivers are decreasing, extending their dry season and transforming them into intermittent or even ephemeral rivers in the short term (Larned et al., 2010). These flow variations can be more drastic in areas with a Mediterranean climate (Larned et al., 2010; Acuña et al., 2014; Creed et al., 2017) such as Chile (Vicuña et al., 2012; IPCC 2014), where, according to modeling, the flows of some rivers could decrease by up to 45% (Stehr et al., 2010).

IRES are characterized by abrupt hydrological changes, with large flows during winter and cessation of flows for days or months in summer. During flow seasons, IRES receive, transport and process organic matter from the drainage basin, as perennial rivers do, whereas dry seasons favor the accumulation of allochthonous organic matter in intermittent river beds (Maamri et al., 1994; Corti et al., 2011). This accumulation is related to river morphology, characteristics of the river bed substrates, physical properties of organic matter and hydrology (Hoover et al., 2006; Richardson et al., 2009). Thus, surface and underground flows influence the abundance of flora and the types present. For example, streams with deeper groundwater levels have more shrub cover and less forest cover, affecting the production of leaf litter and the concentration of inorganic nitrogen in the soil (Lite & Stromberg 2005; Shah & Dahm 2008).

Organic matter input depends on forest structure, composition and phenology (González et al., 2018). For example, in *Eucalyptus* forests, both the input of different types and qualities of leaf litter and nutrient contributions are reduced compared with mixed deciduous forests (Molinero et al., 1996; Pozo et al., 1997; Bunn 1988). Abiotic factors such as rainfall or summer droughts can also influence the quantity and quality of leaf litter (Benfield 1997; Marchin et al., 2010; Sanpera-Calbet et al., 2016), and it has even been proved that latitude is an important predictor of leaf litter quality, which would increase at higher latitudes and decrease toward the equator (Boyero et al., 2017). Furthermore, a recent study showed the organic matter process is faster at low latitudes (Tiegs et al., 2019).

Once organic matter enters rivers, it is chemically and physically transformed (Gessner et al., 1999). This accumulation and decomposition process is mediated by climate and increases under humid and warm conditions (Aerts 1997; Cornwell et al., 2008; Salinas et al., 2011; Campeche et al., 2018; Datry et al., 2018). On another note, the physical and chemical defenses of leaves such as waxes and polyphenols can remain active for a long time, preventing decomposition (Stout 1989; Coq et al., 2010). This leads to diminished CPOM input, affecting the nutrient cycle and productivity of the system (Graça et al., 2015).

In intermittent rivers, summer water shortages reduce microbial activity, end organic matter leaching and interrupt aquatic macroinvertebrate colonization (Larned et al., 2010). By contrast, photodegradation is promoted as a result of increased exposure to the action of ultraviolet radiation and the presence of terrestrial consumers increases (Austin & Vivanco 2006; Corti & Datry 2012). Meanwhile, autumn frost periods could promote the decomposition process and increase the quality of organic matter (Keskitalo et al., 2005; Marchin et al., 2010). Once the drought is over and the reconnection to the fluvial continuum established, all the material that was accumulated and transformed during the dry phase is mobilized and transported (Rosado et al., 2015). This organic matter is transformed into an essential source of carbon and nutrients for downstream heterotrophic organisms (Larned et al., 2010). During the first flood pulses, excess material can cause adverse effects, such as stress in aquatic biota or eutrophication and hypoxia, which sometimes cause the death of fishes, macroinvertebrates and other aquatic organisms (Bunn et al., 2006; Hladyz et al., 2011). Therefore, the first flood pulses can cause little understood intermediate disruptions (Dayton 1971; Connell 1978; Prat et al., 1986; Flecker & Feifareck´s 1994), with effects that could be catastrophic and require restorative mechanisms (Tzoraki et al., 2007; Obermann et al., 2009; Creed et al., 2017). Disruptions caused by flow variation are more significant in Mediterranean rivers and crucial in the regulation of biotic variables (Gasith & Resh 1999). Furthermore, the number of intermittent rivers will increase over time (Larned et al., 2010; Acuña et al., 2014), as will the input of organic matter accumulated in the beds of these rivers (Datry et al., 2018). Accumulated organic matter has been recognized as an important source of nutrients (Shumilova et al., 2019) and global carbon emissions (Datry et al., 2018), which until now have been underestimated; more research on this is matter required. Specifically, the studied basin provides diverse ecosystem services to towns and isolated houses located near the studied rivers. Groundwater abstraction is carried out through deep wells for the benefit of the agriculture, animals, villages and the forestry industry. Meanwhile, surface water is directly used by the animals of the people living in the basin. Given the local importance of intermittent rivers in Mediterranean Chile to local economic activities and the biogeochemical importance of organic matter that accumulates in their beds during the dry phase, the objective of this study was to compare the quantities and types of organic matter that accumulates during the dry season in the intermittent and perennial river beds of Mediterranean Chile.

The field sampling, laboratory analysis and preparation of this article were carried out with the support of students from the Concepción Chiguayante School (Chile). Citizen science is a research collaboration that involves the participation of the public in scientific research activities at different levels, since the data collection methodologies are simple and the activities can have significant impacts on the people involved (Dickinson et al., 2015; Tejeda & Medrano 2018). This approach promotes critical and scientific thinking among the participants and changes perspectives on the natural environment (Phillips et al., 2015). The present research was performed within the framework of a National Commission for Scientific and Technological Research (CONICYT) EXPLORA project, an initiative created by the Chilean government in 1990 to promote the social dissemination of science and technology and strengthen bonds between the scientific community and schools (Prenafeta 2008; Villarroel et al., 2013).

Methodology

As mentioned, the objective of this study was to compare the quantities and types of organic matter that accumulates during the dry season in intermittent and perennial river beds of Mediterranean Chile.

The Lonquén River basin is located in the dryland of the Coastal Mountains in central Chile (36° 25' 59,88'' S; 72° 42' 0'' E). The river is predominantly intermittent, but there are some perennial streams in the basin (Duissaillant 2009). The basin has an irregular shape and drains an area of 1,075 km^2 (Fig. 1). Its geomorphology is heavily weathered and of old relief, with granitic rocks and metamorphic slates. Its soils are eroded, with little permeability and high silt, clay and sand content (Duissaillant 2009). The catchment land use comprises mainly forest plantation (*Pinus radiata* and *Eucalyptus globulus*) and agricultural monocultures, which are typical of the Mediterranean climate of Chile (Becerra 2016; Hernández et al., 2016; Garfias et al., 2018). The annual average temperature is 14.1°C and annual rainfall is 897.9 mm (Duissaillant 2009). The study area rainfall data was collected from the San Agustín de Puñual weather station (code 08118004-0) of the Chilean General Water Directorate (2019) (DGA, for its initials in Spanish).

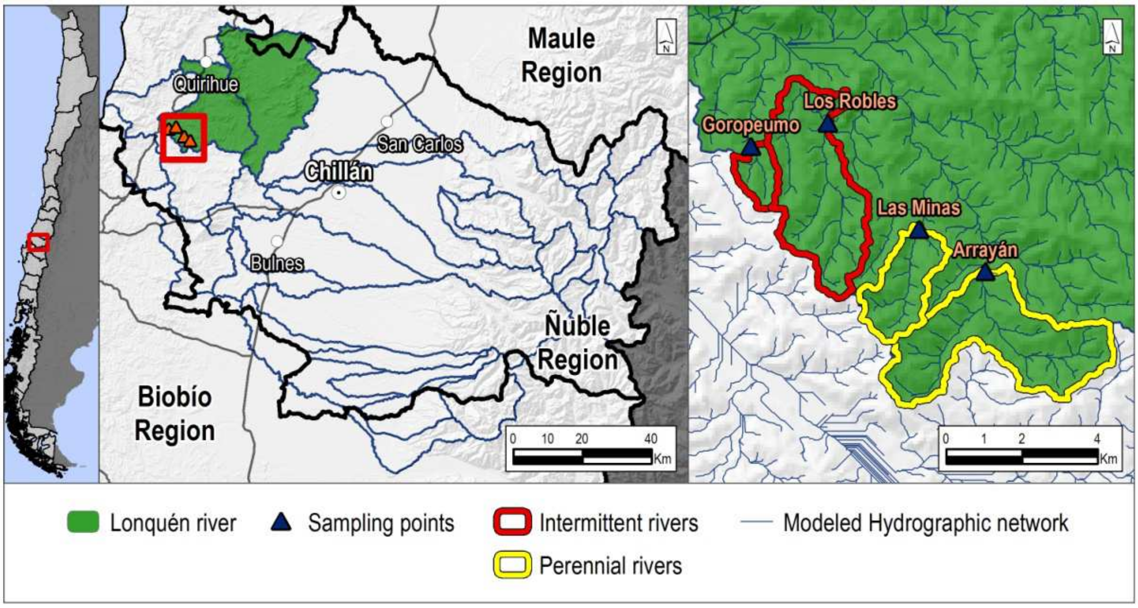

Figure 1. Study area.

CPOM larger than 1 mm was collected by students from the beds of two perennial rivers (Goropeumo and Los Robles) and two intermittent rivers (Las Minas and Arrayán) at the beginning of autumn on May 24, 2017, during the dry phase of the intermittent rivers (Fig. 1). The sampling date was chosen in order to have a maximum of days since senescence and thus the greatest possible CPOM accumulation before the reconnection of the aquatic system. At the time of the sampling, the air temperature was 18°C and the intermittent rivers had no water flow, while both perennial rivers had a baseflow of 0.3 $m^3 s^{-1}$, which was determined using the speed-area method. There was only one sampling season, since the students were involved in Explora CONICYT activities for just one year and the following year the opportunity to participate in another project would be given to a different group of students.

Prior to the collection, students attended three training sessions on intermittent rivers, biogeochemistry and sampling techniques. A section ten times longer than the active average width (see Table 1) of the channel was sampled in order to ensure a consistent sampling effort and obtain representative samples of each reach (Lamberti et al., 2017). To this end, m^2 quadrants were used, with collection in at least the 5% of the entire area; thus, twelve randomly distributed samplings of each reach were carried out (Datry et al., 2018). CPOM was collected by hand and stored in properly labeled airtight plastic bags. The types of CPOM collected were leaves, smaller organic matter ($CPOM_{ms}$, corresponding to 1mm<CPOM<30mm fragments, predominantly pieces of decomposing leaves and plant material), woods, seeds, herbs, shrubs and others (insects and fungi). In the laboratory the wet samples of each CPOM type contained in paper bags were weighed, and subsequently the bags were put into a Memmert oven for 48 hours. The bags were then weighed again to determine the water content percentage. In order to identify the rivers with greater productive potential, an equation was defined,

$$CPOM_{productivity}=CPOM_{ms}/CPOM_{total} \quad (1)$$

With values close to 1 indicating greater productive potential of the ecosystem. For the characterization of the study area, the soil uses of each micro-basin were identified and modeled based on data from 2015 provided by CONAF (CONAF 2017) by means of Arcgis 10.1 software. In order to characterize the riparian vegetation of the studied reaches, photointerpretation was used after anchoring, correction and georeferencing of images. A radius of 50 m around the channel and an area of influence of up to 300 m upstream of each sampled reach were defined. Thus, the vegetation that could affect the deposition of plant material in the studied reaches was included.

To determine if there were significant differences between CPOM, $CPOM_{productivity}$(1) and soil classifications according to photointerpretation results, the Shapiro & Wilk normality test was applied, but as the data had a non-normal distribution, the Kruskal-Wallis nonparametric method was used ($p<0.05$). To examine the relationship between CPOM classifications and moisture in perennial and intermittent rivers, Spearman's correlation was used. All analyses were performed with R software version 3.1.1 using Vegan and Performance Analysis packages.

Results

Weather data indicated low rainfall during summer: 0 mm in January, 8.3 in February, 17.7 mm in March, 26.6 mm in April and 84.3 in May, prior to the sampling.

According to the characterization of the study area, the predominant land uses in the four micro-basins were forest plantations, followed by shrubs and agriculture (70%, 15.8% and 11.3% on average, respectively) (Table 1, Fig. 1 and Fig 2), with agriculture predominant along the middle reaches. In accordance with the photointerpretation (Fig. 2), when comparing the soil uses along intermittent and perennial rivers (reach and its influence area included), significant differences were not found ($p>0.05$).

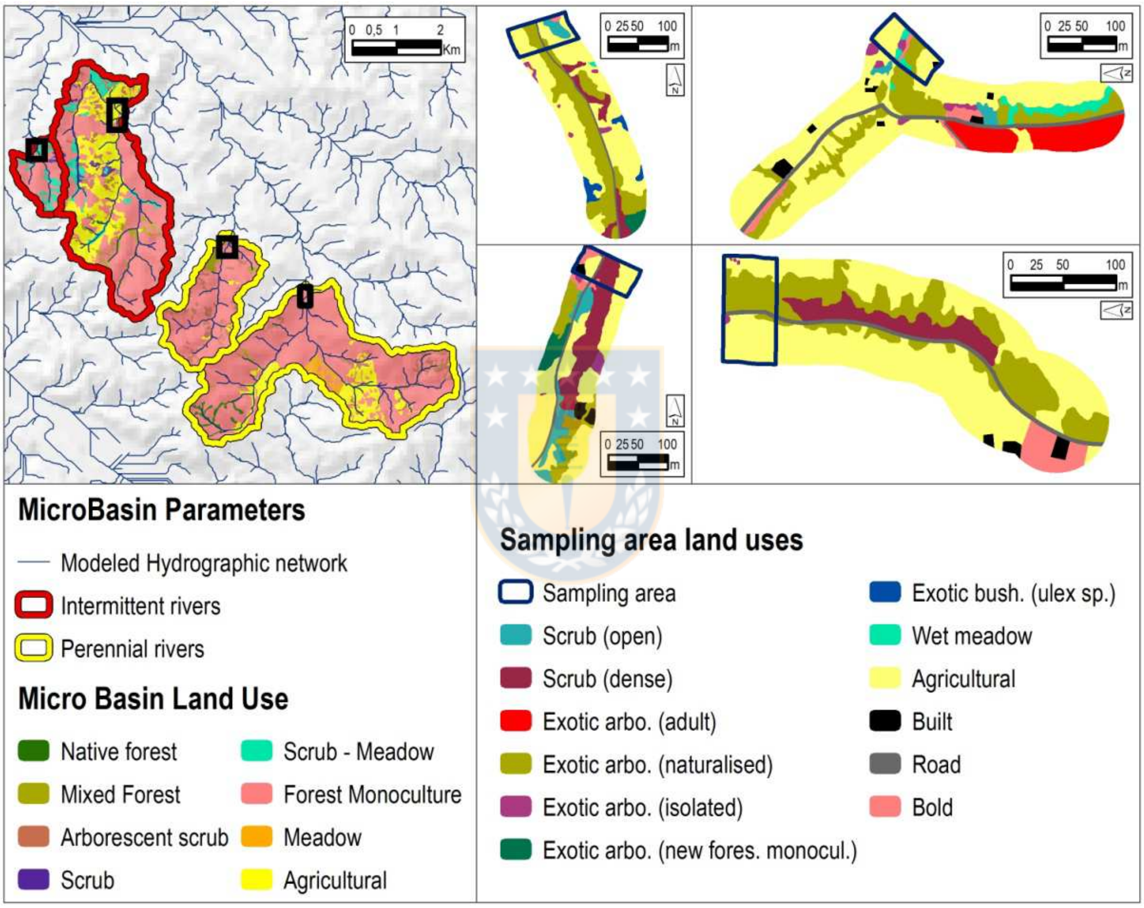

Figure 2. Soil uses of the microbasins and photointerpretation of the sampled reaches and its influence area (CONAF 2017).

Regarding CPOM, intermittent rivers accumulated organic matter with higher productive potential for the ecosystem ($CPOM_{productivity}$, $p<0.5$) and in greater quantities (1,029 g m^{-2}) than perennial rivers (337 g m^{-2}, $p<0.05$) (see Table 1 and Fig. 3). The difference is thought to be due to a larger quantity of leaves, $CPOM_{ms}$, seeds, herbs and shrubs in the intermittent rivers. Additionally, no significant differences in wood and other types of organic matter were found ($p>0.05$). Furthermore, no herbs or shrubs were found along either perennial river (Fig. 3). $CPOM_{productivity}$ in both intermittent rivers was identical, as was the case in perennial rivers (p>0.05) (see Table 1).

No relationship between the moisture of the organic matter and the types of CPOM was found in any river. In intermittent rivers, there was a strong relationship (p>0.05) between different types of organic matter, especially between $CPOM_{ms}$ and wood, in contrast to the perennial rivers, in which only a relationship between leaves and $CPOM_{ms}$ was observed (Fig. 4).

Table 1 Soil use of the microbasins, photointerpretation of the reach, including influence area, and characteristics of the studied riverbeds in the Lonquén river basin.

		Intermittent		Perennial	
		Goropeumo	**Los Robles**	**Las Minas**	**Arrayan**
Land use (%)	Area (ha)	135.0	954.0	378.0	1084.0
	Forest plantation	66.0	56.6	81.5	76.8
	Farming	0.2	27.9	1.5	15.9
	Shrubs	33.7	12.4	12.4	4.7
	Native forest	0.0	0.2	0.0	2.2
	Exotic forest	0.0	2.9	4.6	0.4
Photointerpretation (%)	Area (ha)	3.9	6.8	3.9	3.9
	Agricultural	49.9	52.5	42.5	53.5
	Exotic wild trees	30.6	17.6	11.4	27.5
	Exotic monoculture trees	2.2	0.0	4.2	0.0
	Exotic trees isolated	1.5	1.6	2.0	0.2
	Exotic trees adult	0.0	11.9	0.0	0.0
	Exotic shrub (Ulex spp)	3.1	0.0	0.0	0.0
	Shrubs-matorral	8.8	1.5	30.2	8.8
	Hygrophilous	0.2	4.1	0.0	0.0
	Roads	3.1	6.2	4.0	4.1
	Edification	0.0	1.9	2.9	1.5
	Fallow land	0.5	2.7	2.8	4.4
Streambed	Visual coverage of riparian vegetation (%)	90.0	80.0	95.0	95.0
	Active channel width (m)	2.0	4.0	5.0	4.0
	Floodplain width (m)	10.0	10.0	10.0	7.0
	Silt (%)	70.0	20.0	0.0	90.0
	Sand (%)	30.0	80.0	100.0	10.0
	$CPOM_{productivity}$	0.5	0.5	0.3	0.1
	CPOM moisture (%)	50.4	45.5	47.5	40.0

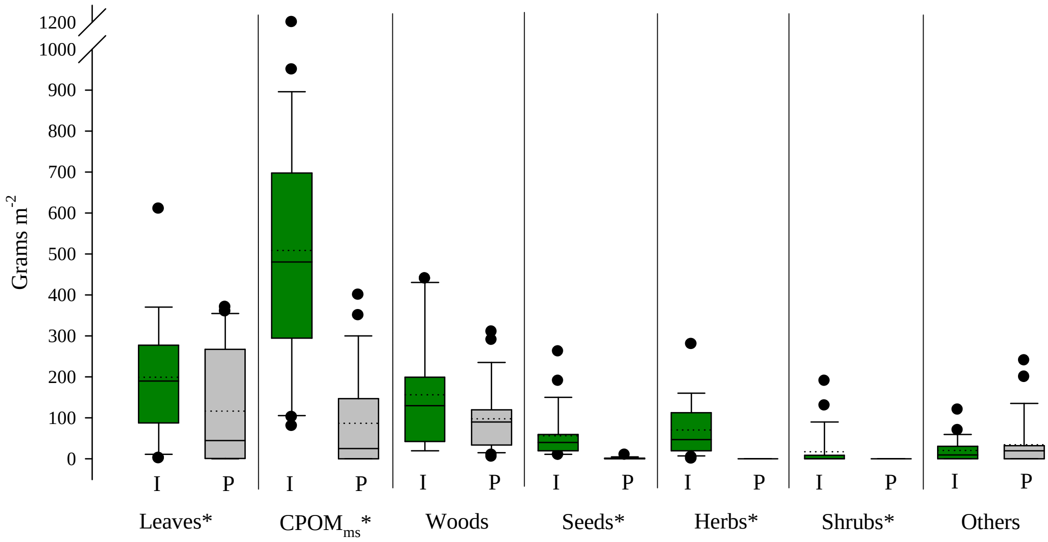

Figure 3. Coarse particulate organic matter (CPOM) sampled in intermittent rives (I, green color) and perennial rivers (P, gray color),* p value< 0.05. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles; mean values are shown with a dotted line).

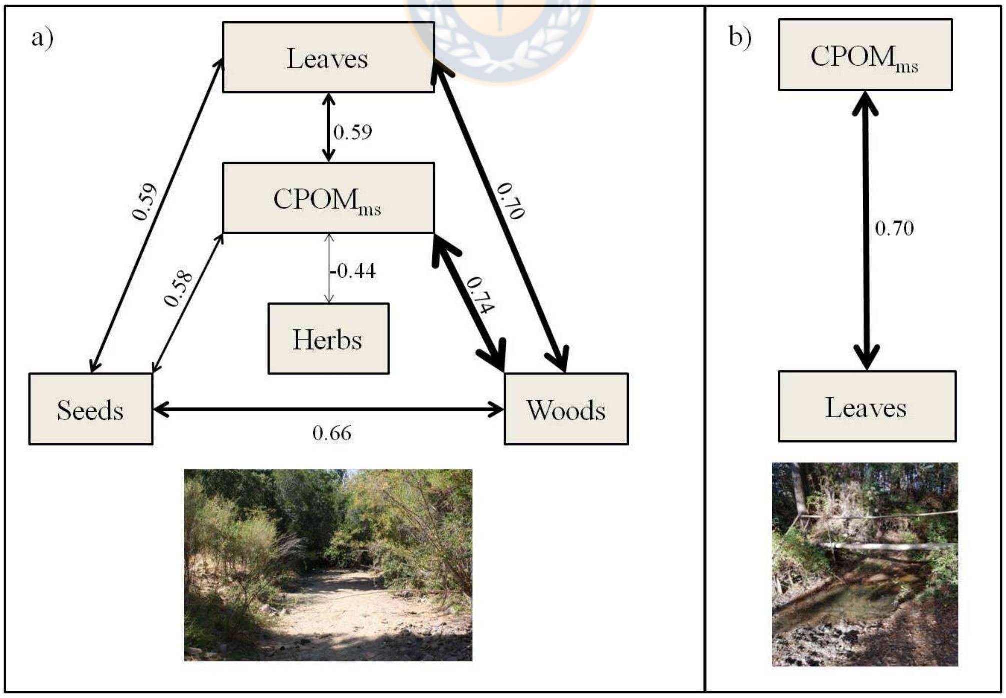

Figure 4. Relations of the coarse particulate organic matter in intermittent (a) and perennial (b) rivers. Arrows and numbers indicate significant relation and r value, respectively.

Discussion

Low-order rivers drain small hydrographic networks and have narrow channels bordered by abundant riparian vegetation (Webster & Meyer 1997; Gessner et al., 1999; Raymond et al., 2013; Hasler et al., 2016). Therefore, organic matter is processed within the channel and transported downstream, where it continues to be processed along the longitudinal profile (Vannote et al., 1980). However, it also happens that most low-order rivers in Mediterranean climates have intermittent behavior (Benstead & Leigh 2012) and therefore are crucial in the regulation and processing of organic matter, since the climate and latitude are the key factors that determine the characteristics of the riparian area, type of vegetation, flow regime and biomass input (Lamberti et al. 2017; Datry et al., 2018; Tiegs et al., 2019). This ultimately impacts the accumulation and decomposition of organic matter (Datry et al., 2018). In contrast to perennial rivers, intermittent rivers accumulate this material to a greater extent, subjecting it to photodegradation and/or biodegradation, according to humidity and light conditions in the river bed (Austin & Vivanco 2006; Corti & Datry 2012).

The results indicated that there was a greater accumulation of CPOM, especially of a smaller size, in intermittent river beds and that it had higher productive potential and more complex relationships with the different types of organic matter, even when the land use of the basins, river order, morphology, substrate, physical properties and vegetation characteristics were similar in both types of rivers. Therefore, the variable that most affected the accumulation of organic matter in this study was hydrology. Similar results were observed by Hoover et al. (2006) and Richardson et al. (2009); in these studies, hydrology, river channel characteristics and physical properties of the plant material are involved in CPOM retention and decomposition. In this sense, surface and underground water flow can limit the growth of different types of vegetation (Shafroth et al., 2000). Thus, in the perennial rivers, although they receive allochthonous material, the continuous flow throughout the hydrological year reduced the accumulation of plant material, which made the growth of herbs and shrubs in the river bed impossible, limiting the relationships among types of organic matter. The accumulation of plant material was highly dependent on the leaves provided by riparian vegetation that can decompose and generate bioavailable organic matter. This took place through processes that include biotic factors, such as benthic macroinvertebrates, bacteria and other physical factors that are related to geomorphology (for example, pools and riffles), water velocity in the reach and even climate and latitude (Vannote et al., 1980; Cummins et al., 1980; 1984; Datry et al., 2018; Tiegs et al., 2019).

The studied reaches in the intermittent and perennial rivers presented high CPOM moisture (*ca.* 50%) and high riparian coverage, which promoted the generation of shade in the river bed. These conditions favored bacterial decomposition of organic matter in the intermittent rivers during the season without flows, which was also favored by rainfall prior to sampling. Moisture can be maintained in piles of wood and CPOM, predominantly of larger sizes (Pettit et al., 2006). In addition, in the intermittent rivers there was a higher amount of CPOM and decomposing organic matter, even though based on a visual examination there appeared to be a greater percentage of riparian coverage in the perennial reaches and the photointerpretation analyses indicated a similar soil use classification (Fig. 2). This showed that intermittent rivers follow other biogeochemical pathways than those described in classical processes, since water flow transports solutes and particulate organic matter downstream and toward the coastal area, especially in the first flood pulses (Datry et al., 2018), and then acts as a longitudinal biogeochemical reactor that rapidly processes this material, as Vannote et al. (1980) describe. However, particularly in intermittent rivers, bacteria that are involved in processing are highly adapted to extreme water conditions and to the cessation of flow/rewetting (Austin et al.,2004; Sponseller 2007). During droughts, meanwhile, most of the little processing in river beds is mediated by photodegradation, and there is isolated processing in pools by macroinvertebrates and microbial activity (Larned et al., 2010). Therefore, biological participation is high (e.g., microorganisms and shredder macroinvertebrates), since intermittent rivers are critical sites for the accumulation of organic matter that has the potential to generate large-scale point pulses downstream in the first flood pulse, as well as high emissions of CO_2 into the atmosphere. For example, Rosado et al. 2015 and Datry et al. 2018 found up to 13 g m^{-2} d^{-1} CO_2 emissions into the atmosphere. The Mediterranean IRES of central Chile sampled in this study were included in the *1000* Intermittent Rivers *project (Datry et al., 2018)*.

In summer and autumn periods without flows, the transformation of organic matter slows and the material accumulates (Austin & Vivanco 2006; Foulquier et al., 2015). Consequently, this material with low processing rates and higher-quantity labile and bioavailable matter (Corti et al., 2011) is exported to the watercourse when the flow of the rivers restarts(Larned et al., 2010, Corti & Datry 2012; Raymond et al., 2016), a phenomenon that was studied by Casas-Ruíz et al. (2017) to determine when the river acted as an active reactor or passive tubing in the processing of dissolved organic matter. The opposite takes place in perennial rivers, which transport organic material from the riparian vegetation with low levels of processing and continuous CPOM renewal.

According to the results of previous studies (Benfield 1997; Austin & Vivanco 2006; Marchin et al., 2010; Corti & Datry 2012; Sanpera-Calbet et al., 2016), drought affected both the decomposition and quality of organic matter due to a higher carbon:nitrogen molar ratio in the leaf litter, a decrease in microbial activity and an interruption of organic matter colonization, and in the IRES studied, it is assumed that the summer drought of 2017 also affected the accumulated CPOM. Despite this phenomenon, a large amount of decomposing organic matter was found, probably associated with the moisture content of the samples after a wet autumn (Aerts 1997; Gholz et al., 2000; Keskitalo et al., 2005; Marchin et al., 2010; Salinas et al., 2011). This, together with the latitude of the rivers, favors the formation of good quality organic matter. In a global study, Boyero et al. (2017) found that in the tropics leaf litter is of lower quality and phosphorous is limiting, which restricts decomposition by detritivores, unlike what happens at higher latitudes. Therefore, the results indicate, on one hand, the importance of IRES in the functioning of aquatic ecosystems during the first flood pulses and indicates the high potential of these rivers as a source of carbon, organic matter and energy for the productivity of the ecosystem (Gessner et al., 1999; Raymond et al., 2013; Graça et al., 2015). On the other hand, perennial rivers accumulate less allochthonous organic matter and transport it continuously, which is important at critical moments (spring-summer) when high energy inputs are required.

IRES should be analyzed in a climate change context, since these rivers are increasingly expanding in both length and area (Gleick 2003; Larned et al., 2010; Acuña et al., 2014). What is more, perennial rivers are at risk of undergoing hydrology and water quality modifications (Stehr et al., 2010; Vicuña et al., 2012; Yevenes et al., 2018) and thus of becoming intermittent. The results of this study, the first in the region, were consistent, although further data are required, and the support of the public may prove important. There is great interest in Chile in science- and technology-related environmental issues, but both the dissemination of techno-scientific knowledge and understanding of the scientific method are deficient (Prenafreta 2008; Villarroel et al., 2013). Therefore, it is essential to promote initiatives that involve science and citizens. This study acquainted students with the scientific method, enabling them to view intermittent rivers not as temporarily dead systems, but rather as systems of local and global importance in the ecosystem. Students shared their results and what they learned in the Provincial and Regional Science and Technology Congress organized by EXPLORA (CONICYT) and in the National Science and Technology Fair at Biobío University, Chile.

Conclusions

Intermittent rivers can accumulate greater quantities of CPOM with a higher productive potential than perennial rivers. According to previous studies, the organic matter that accumulates generates downstream nutrient emissions and CO_2 emissions into the atmosphere in the first flood pulses. In addition, more than half of the global fluvial network is made up of intermittent rivers and it is predicted that they will increase in quantity and length, especially in areas with a Mediterranean climate. Therefore, it is important to study the amount and type of CPOM that these rivers can accumulate to determine the consequences of the first flood pulses. Research in larger geographical areas in collaboration with citizens, to foster a deeper knowledge of intermittent rivers, is recommended.

Authors' contributions

KB, CA, JF and AH contributed to the design of the work, sampling, analysis, interpretation of results and writing of the work. KS and JF analyzed and interpreted the statistical and geospatial data, respectively. FP, AB, MY and RF reviewed the work and participated in the writing. All authors read and approved the final manuscript and have agreed to be personally responsible for their own contributions.

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List of abbreviations
CPOM: coarse particulate organic matter
IRES: intermittent rivers and ephemeral streams
CONICYT: National Commission for Scientific and Technological Research

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CAPÍTULO II: A global analysis of terrestrial plant litter dynamics in non-perennial waterways

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Author's contributions
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Abstract

Perennial rivers and streams make a disproportionate contribution to global carbon (C) cycling. However, the contribution of intermittent rivers and ephemeral streams (IRES), which sometimes cease to flow and can dry completely, is largely ignored although they may represent over half the global river network. Substantial amounts of terrestrial plant litter may accumulate in dry IRES and, upon rewetting, this material can undergo rapid microbial processing. We present the results of a global research collaboration which collected and analyzed terrestrial plant litter from 212 IRES reaches spanning major environmental gradients and climate zones. We assessed litter decomposability by quantifying the litter C-to-nitrogen ratio (C:N) and oxygen (O_2) consumption in standardized assays and estimated potential short-term CO_2 emissions during rewetting events. Aridity, cover of riparian vegetation, channel width, and dry phase duration explained most variability in the quantity and decomposability of plant litter in IRES. Our estimates indicate that IRES could contribute up to 10% of stream and river CO_2 evasion, through pulses of CO_2 emission upon litter rewetting, particularly from temperate climates. Incorporation of IRES has become vital to improve the accuracy of global C cycling assessments.

Keywords: global change, river ecosystem functioning, CO_2 emissions, temporary rivers, riparian vegetation, C cycle.

Introduction

Decomposition of terrestrial plant litter is an essential, biosphere-scale ecosystem process (Boyero et al., 2011). Of 120 Pg of organic C produced by terrestrial plants annually, about half is respired by the plants but only a small fraction is removed by herbivores, so that up to 60 Pg enter the dead organic matter pool (Beer et al., 2010; Boyero et al., 2011). Fresh waters make a disproportionate contribution to global C cycling through terrestrial plant litter (TPL) decomposition and atmospheric CO_2 emissions (Raymond et al., 2013; Hotchkiss et al., 2015). This contribution is particularly apparent in perennial rivers and streams, where water and nutrient availability stimulate rapid decomposition by microbes and invertebrate detritivores (Gessner et al., 2010; Boyero et al., 2011; Raymond et al., 2013). TPL deposited in fresh waters, and the release of its decomposition products, are critical energy sources that support food webs and ecosystem processes, including key C cycling pathways (Gessner et al., 2010; Boyero et al., 2011).

A major shortcoming of current estimates of the contribution of rivers and streams to global C cycling (Battin et al., 2009; Raymond et al., 2013; Butman et al., 2016) is the omission of IRES, in which drying and rewetting events create ecosystems that transition between terrestrial and aquatic phases (Stanley et al., 1997; Datry et al., 2016; Larned et al., 2010). IRES are widespread ecosystems draining a large proportion of terrestrial biomes across all continents and climate types (Stanley et al., 1997; Larned et al., 2010; Datry et al., 2014; Acuña et al., 2014). Moreover, IRES are increasing in extent due to global change (Jaeger et al., 2014; Datry et al., 2016;). During the dry phase, TPL deposited on the riverbed accumulates, decomposing only slowly through photodegradation and terrestrial decomposer activity (Foulquier et al., 2015; Austin & Vivanco 2006). Then, when flow resumes, the accumulated material is mobilised and transported downstream (Corti & Datry 2012). Concentrations of with particulate and dissolved organic matter in advancing wetted fronts exceed baseflow concentrations by several orders of magnitude (Corti & Datry 2012). IRES have therefore been conceptualized as punctuated biogeochemical reactors (Larned et al., 2010).

To understand the role of IRES in global C cycling, global-scale data are needed to characterize the variables controlling TPL accumulation in dry channels and its decomposability upon flow resumption. Climate influences the type and productivity of riparian vegetation (Michaletz et al., 2014) and the flow regimes of IRES (Foulquier et al., 2015; Datry et al., 2016). Channel topography and flow conditions, including the timing and duration of dry periods(Foulquier et al., 2015), control TPL deposition and retention, with wide channels receiving proportionally less riparian material than narrow ones (Ehrman & Lamberti 1992). TPL decomposability is typically altered during dry phases, due to partial degradation or leaching of labile constituents, relative accumulation of recalcitrant compounds, and impoverishment of nutrients in terrestrial conditions (Austin & Vivanco 2006; Boyero et al., 2017). Therefore, we predict that TPL accumulation and decomposability would be a function of climate, riparian vegetation, channel topography, and duration of the dry phase (Fig. 1). We explored these relationships by assessing the quantity and decomposability of accumulated TPL in 212 dry river channels located in 22 countries distributed across wide environmental gradients and multiple climate zones (Datry et al., 2016).

Methods

Sampling design

Terrestrial plant litter (TPL) deposited on dry riverbeds was collected by participants of an international consortium (http://1000_intermittent_rivers_project.irstea.fr[1]) following a standardised protocol (Datry et al., 2016). In total, 206 near-natural river reaches were studied in 22 countries spanning 13 Köppen-Geiger climate classes. Briefly, the sampled river reaches were 10 × the average active channel widths to cover a representative area of each river channel and to ensure consistent sampling effort across reaches (Leopold 1966). The active channel was defined as the area of frequently inundated and exposed riverbed sediments between established edges of perennial, terrestrial vegetation and/or abrupt changes in slope (Gordon et al., 2004). TPL was collected by hand from 1 m^2 quadrats placed randomly within each reach during a dry phase. The quadrats covered ~5% of the reach surface area (e.g. five quadrats in a 100 m^2 reach). Different types of TPL (i.e. leaves, wood, fruits, catkins, herbs) were stored in separate airtight plastic bags.

Environmental variables

A set of 22 environmental variables reflecting reach characteristics at different spatial scales was estimated or calculated for each site. Seventeen variables were determined locally. Mean annual temperature and precipitation were extracted from the WorldClim.org database, which gives 1-km spatial resolution climate surfaces for global land areas over the period 1970-2000. Mean annual potential evapotranspiration (PET) and mean annual aridity were determined using the Global Aridity and PET database published by the Consortium for Spatial Information (CGIARCSI, http://www.cgiar-csi.org) using the WorldClim.org database.

PET is a measure of the ability of the atmosphere to remove water through evapotranspiration and was calculated as a function of annual mean temperature, daily temperature range and extra-terrestrial radiation between 1950 and 2000. Mean annual aridity was assessed using an aridity index (UNEP 1997) and expressed as 1 000 × precipitation / PET between 1950 and 2000. Aridity index values were high in humid and low in arid conditions.

Climate zones following the Köppen-Geiger system were determined from the global climate map derived from long-term monthly precipitation and temperature time series in a grid of weather stations and interpolated among stations using a two-dimensional (latitude and longitude) thin-plate spline with tension onto a 0.1° by 0.1° grid for each continent (Peel et al., 2007). Last, we estimated time since leaf abscission as the time between the estimated onset of leaf senescence and the sampling date. Although leaf fall is more continuous marked in tropical areas than in other climate zones, to facilitate comparison among sites, onset of leaf senescence was set to the 1st of September and the 15th of February in the northern and southern hemispheres, respectively (Estiarte & Peñuelas 2015).

Litter drying, weighing and grinding

TPL was transported to local laboratories within 8 h of collection when possible and oven dried at 60 °C for ≥12 h (<24 h for leaves). Fresh material such as fruits or wood was dried at room temperature for 1 week before oven drying. The dried material was weighed to the nearest gram.

Although wood can account for considerable volumes of TPL deposited in riverbeds, it is far more recalcitrant than leaf litter (LL). Therefore, we focused on LL in our assessment of TPL decomposability during short-term rewetting events. LL was thoroughly mixed before taking a 60-g subsample that was first shredded by hand and passed through a 0.5-cm mesh screen, then shipped to the IRSTEA laboratory (Lyon, France) for further processing.

Decomposability of leaf litter

Laboratory measurements can provide a useful means to address global-scale environmental research questions (Benton et al., 2007) and overcome the current data shortage on intermittent rivers and ephemeral streams. In particular, they facilitate tests of between-reach variability in O_2 consumption rates in a standardised way and identification of the primary drivers responsible for the observed variability. Although we did not quantify decomposition rates directly, we assessed two proxies of LL decomposability, the C:N mass ratio and oxygen (O_2) consumption rate after rewetting.

Three 10-mg LL subsamples were taken from each sample, ground to 5 μm with a ball mill (MM301, Retsch GmbH, Haan, Germany) and the C:N ratio determined with an elemental analyzer (FlashEA 1112, Fisher Scientific, Waltham, Massachusetts, USA). O_2 consumption was determined in respiration flasks placed in a climatic room at 20 °C. LL subsamples were processed in 10 successive batches of 25-50 subsamples. Each batch was incubated in three 200-L polyethylene containers filled with tap water at room temperature to prevent O_2 exchange with the atmosphere. For each subsample, two analytical replicates were processed by placing 0.1 g LL into 250-mL glass respiration flasks filled with Volvic® mineral water, then sealed airtight using a 3.2-mm-thick silicon-PTFE septum and a cut-out open-top cap. Care was taken to ensure air bubbles were excluded. O_2 concentrations were measured with a needle-based micro-optode (Oxygen Microsensor PM-PSt7; PreSens, Regensburg, Germany) using a stand-alone, portable, fiber-optic O_2 meter (Microx 4 trace; PreSens, Regensburg, Germany). Incubations were run for approximately 24 h (range of incubation times: 23.4-25.8 h; mean ± S.D. = 24.3 ± 2.0 h) to simulate short-term rewetting events. We used LL communities as a source of microbes, because dry LL hosts dormant communities can quickly resume activity after rewetting litter (Mora-Gómez et al., 2018). We also ran tests to ensure our oxygen consumption rates were realistic. This was achieved by using LL, different sources of water with and without a standard inoculum from local streams (see below).

O_2 concentrations were measured twice, 2 h and 24 h after the respiration flasks were filled with water. We waited for 2 h before taking the first measurement to allow gas release from air-saturated pores within the LL (Dorca-Fornell et al., 2013). Although the respiration flasks were carefully filled without bubbling the water, we left them open for 2 h while the LL released gas, to ensure that O_2 concentration was saturated, but not supersaturated to avoid a notable underestimation of respiration rates over 24 h. Flasks were gently agitated every 6 h during the incubation period and before each measurement to ensure homogenous O_2 concentrations in the water. For each batch, O_2 concentrations were also measured in three control respiration flasks filled with Volvic® mineral water only. Microbial respiration associated with LL (R: mg O_2 g^{-1} LL dry mass h^{-1}) was calculated as:

$$R = \frac{\frac{\left(O_{2sample}^{2h} - O_{2sample}^{24h}\right) - \left(O_{2control}^{2h} - O_{2control}^{24h}\right)}{incubation\ time(h)} \times respiration\ flask\ volume}{(g)}$$

Where O_2 is the dissolved O_2 concentration (mg L^{-1}); the subscripts sample and control refer to each analytical replicate and the mean O_2 of the three control respiration flasks; and the superscripts 2 h and 24 h correspond to the O_2 concentrations measured 2 h and 24 h after the flask was filled, respectively. *R* was then standardised to 20 °C to correct for small (i.e., ± 1.1°C) temperature variations during the measurements, assuming that O_2 consumption rates double with a temperature increase of 10 °C (Davidson & Janssens 2006). The mean of the two analytical replicates was used as a measure of microbial respiration associated with LL rewetting for each sample. For 10 samples, we had not sufficient litter material to conduct the respiration measures and for another 5, the material was not adequately processed by the collectors and was thus excluded from the analysis. Hence, the total number of samples analysed was 197.

The total potential CO_2 released per m^2 of riverbed over 24 h after rewetting was estimated by multiplying, for each sampling site, the amount of accumulated LL (in g per m^2) by the rate of O_2 consumption (mg O_2 g^{-1} LL dry mass h^{-1}) over 24h. The obtained estimates of O_2 consumption (mg O_2 m^{-2} day^{-1}) were then converted into CO_2 production (mg CO_2 m^{-2} day^{-1}) by assuming a respiratory quotient of 1 (Dilly 2001).

Sensitivity of O2 consumption measurements

To explore the sensitivity of our laboratory protocol to assess LL respiration in the initial stage of rewetting, we compared O_2 consumption rates with and without a microbial inoculum added. The inoculum was prepared from sediments collected with a shovel from a flowing reach of the Albarine River close to Lyon, France (Foulquier et al., 2015). We added 250 mL of Volvic® water to 250 mL of sediment and placed it twice in an ultrasonic bath (Branson 5510E, Emerson, MO, USA) for 30 s. The suspension of water and sediment was gently shaken after ultrasonication. We then added 2.5 mL of the inoculum suspension to each respiration flask before filling them with Volvic® water. Before adding the inoculum, the suspension was gently shaken again to ensure a uniform inoculum distribution within the flask. In addition, we compared oxygen consumption rates without inoculum by using stream water from three LL collection sites (Albarine, Audeux and Calavon), instead of Volvic® mineral water.

We did not use an inoculum in our final experiments, because: a) it is conceptually problematic to use an inoculum from one system to quantify the decomposability of material from other areas and the large variability induced by doing so could mask large-scale patterns of oxygen consumption rates upon rewetting; b) it was impractical to ask international participants to send 2-3 L of river water to IRSTEA, especially when the rivers were dry; c) it is virtually impossible to keep an inoculum constant among runs in laboratory microcosms. Overall, these results water also indicate that our approach is robust but provides conservative O_2 consumption rates.

Data analysis

We used random forests (RFs) to explore relationships between environmental variables and TPL quantity, LL decomposability, and CO_2 release upon rewetting events. RFs are highly flexible regression techniques suitable for modelling response variables (e.g., the quantity and decomposability of TPL) that show complex relationships with environmental variables (e.g., climate, riparian zone, flow regime, channel topography).

RFs are invariant to monotonic transformations of environmental variables, perform better than other regression techniques when facing multicollinearity, are relatively robust to over-fitting, automatically fit non-linear relationships and high-order interactions, provide an overall goodness-of-fit measure (R^2) and a measure of importance of each variable in a model (Breiman 2001; Pitcher et al., 2012; Leigh & Datry 2017).

The role of environmental variables in RF models can be examined using importance measures and partial dependence plots. Importance measures provide the contribution of variables to model accuracy and are obtained from the degradation in model performance when a predictor is randomly permuted (Breiman 2001; Pitcher et al., 2012). Partial dependence plots show the marginal contribution of a variable to the response (i.e., the response as a function of the variable when the other variables are held at their mean value) and were used to interpret the relationships between predictors and dependent variables (responses), which were $\log_{10}(x+1)$ transformed prior to analyses (Breiman 2001; Pitcher et al., 2012; Leigh & Datry 2017). Sets of global RF models were run for the main dependent variables (quantities of TPL and LL; LL C:N, respiration rate and CO_2 production) and then these RF sets were run for each of three climate zones, using the Köppen-Geiger classification of sampling sites: arid (merging Köppen-Geiger BSh, BSk, BWh and BWk; n=31), temperate (merging Cfa, Cfb, Csa, Csb, Cwa; n=150) and tropical (merging As, Aw; n=19). No RF models were run for alpine and continental climates due to the low number (≤10) of sampling sites.

We ran all global and climate-specific models with and without 'time since senescence' as a predictor to assess the potential of this variable to improve predictive power, despite the large uncertainty of this variable in some climate zones, particularly in the tropics. Removing the variable from the models did not improve or diminish predictive power, including for IRES in the tropics, but since RF models selected it as a strong predictor for most response variables, we decided to include it in the analyses.

Results

Terrestrial plant litter accumulation in dry riverbeds

Our results refine current understanding of the global distribution and variability in TPL accumulation in IRES during dry phases. The quantity of TPL collected in 212 dry riverbeds ranged from 0 to 8291 g m^{-2} (mean $\pm$ S.D. = 284 $\pm$ 794, median = 102 g m^{-2}; Table 1). This material mainly comprised leaf litter (LL) and wood (42% and 39% of the total mass, respectively), whereas herbs, fruits and catkins accounted for <20% of the total mass (Table 1). The quantity of LL ranged from 0-963 g m^{-2} (mean $\pm$ S.D. = 88 $\pm$ 141, median = 36 g m^{-2}).

Table 1: Quantity (g dry mass.m^{-2}) of terrestrial plant litter collected in dry riverbeds (Min: minimum, Max: maximum, Mean, S.D.: standard deviation, Fraction: % of the total quantity.

Type of material	**Min**	**Max**	**Mean**	**S.D.**	**Fraction (%)**
Total plant litter (TPL)	0	8 291	284	805	100
Leaf litter (LL)	0	963	88	141	42
Wood	0	7 812	162	724	39
Herbs	0	500	8	39	6
Fruits	0	327	6	35	5
Catkins	0	351	14	44	5
Miscellaneous	0	41	1	4	2

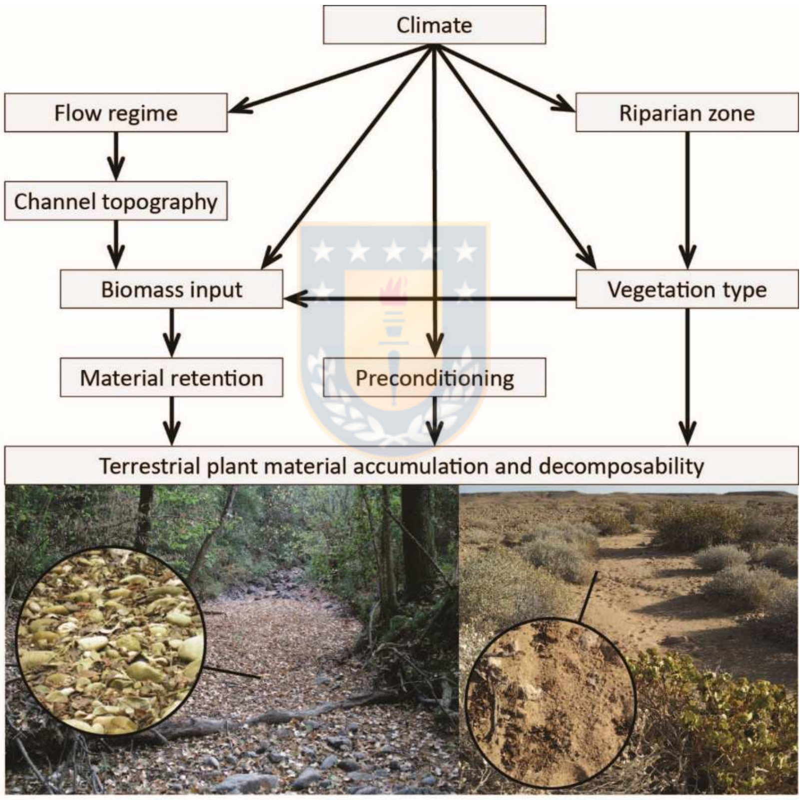

Figure 1. Conceptual model of the main variables predicted to control plant litter accumulation and decomposability in IRES. The accumulation of terrestrial plant material is a function of the input of litter from riparian vegetation mediated by its retention that depends on channel topography and the duration of dry events. Channel topography and composition of the riparian vegetation are driven by flow regimes and, ultimately, climate. Climate also influences the condition of the litter accumulated during dry phases and hence its preconditioning. Photo credits: D. von Schiller (left panel) and M. Moléon (right panel).

Relationships between TPL quantity and environmental variables were assessed using Random Forest models (RF), which are highly flexible regression techniques suitable for modelling responses that show complex relationships with environmental conditions (e.g., climate, riparian zone, flow regime, channel topography). RF based on data from all samples explained 41.4% and 38.3% of the total variance in TPL and LL quantity, respectively (Table 2, Fig. 2).

Supporting our conceptual model (Fig. 1), aridity, mean annual precipitation, catchment area, and dry period duration were the most important predictors of TPL quantity (Table 2). Aridity, river width, riparian cover, time since senescence, and dry period duration were most influential to determine LL accumulation (Table 2). LL quantity generally increased with riparian cover and decreased with river width (Fig. 2). Relationships with time since senescence, aridity, and dry period duration were more complex. LL quantity decreased as the aridity index increased to 250, increased sharply until it reached 650 and then plateaued (Fig. 2). LL quantity also increased almost linearly as dry period duration increased to 200 d, and then dropped sharply (Fig. 2). The quantity of LL fell for 320 days after estimated senescence and then rose slightly (Fig. 2).

The greatest quantity of terrestrial material, in particular LL, was reported from first-order, forested, temperate IRES, suggesting these sites are hotspots of organic matter accumulation in dendritic river networks. These results essentially support the River Continuum Concept (RCC) but differ from its predictions regarding the fate of TPL entering river channels (Vannote et al., 1980). According to the RCC, a large portion of TPL entering forested headwaters is immediately processed by heterotrophic microbes and invertebrate shredders, generating significant amounts of fine-particulate organic matter that is exported downstream. In contrast, we found TPL accumulations in dry channels to be greatly increased compared to perennial rivers (Foulquier et al., 2015; Datry et al., 2016), because the absence of flowing water limits biological activity and physical abrasion. During the initial phases when flow resumes, much of this material can then be transported and further processed downstream(Stanley et al., 1997; Larned et al., 2010; Corti & Datry 2012).

Overall, LL accumulation in IRES matches global patterns in terrestrial inputs (Boyero et al., 2011, 2017), revealing strong biogeochemical and ecological links between rivers and adjacent terrestrial ecosystems. The positive relationship between the degree of aridity and the quantity of accumulated LL probably reflects water-limited riparian plant growth (Olson 1963), while the saturating relationship observed above an index value of 700 suggest that, in humid conditions, LL accumulation becomes limited by other factors. LL quantities in dry channels reflect a balance between riparian and upstream inputs, and losses due to dry-phase decomposition and downstream export during phases of flow. Although our results inform estimates of LL accumulation in dry channels, downstream effects of LL transport and processing when flow resumes will also depend on the decomposability of the accumulated organic matter.

Table 2. Detailed results of global Random Forest models on five response variables. The variables used as predictors are described in Supplementary Material 7. INC MSE corresponds to the increase in the mean squared error of the predictions after permutation. INC Node Purity is the average decrease in node impurity measured as residual sum of squares. Both are used to assess the importance of predictors in an RF model. The higher the value of both measures, the more important the variable.

Response variable	Variance explained (%)	Variable	INC MSE (%)	INC Node Purity
Total terrestrial plant litter (TPL)	41.4	Aridity	31.9	34.9
		Rain	29.1	36.4
		Catchment area	25.3	34.2
		Duration of dry period	19.6	25.7
Leaf litter (LL)	38.3	Aridity	47.4	23.8
.		River channel width	40.8	26.7
		Riparian cover	37.2	23.8
		Time since senescence	30.6	19.1
		Duration of dry period	30.3	26.5
C:N	14.9	PET	63.5	2.9
		Duration of dry period	48.3	2.1
		Riparian cover	47.6	2.1
		Aridity	42.2	2.0
Respiration rate	36.8	Riparian forest	68.6	0.3
		Catchment area	60.5	0.2
		Time since senescence	51.7	0.2
		Duration of dry period	48.2	0.2
		Aridity	38.7	0.1
		C:N	35.2	0.1
CO_2 release	31.9	Time since senescence_	57.7	38.3
		Aridity	49.7	27.3
		Duration of dry period	44.1	36.7

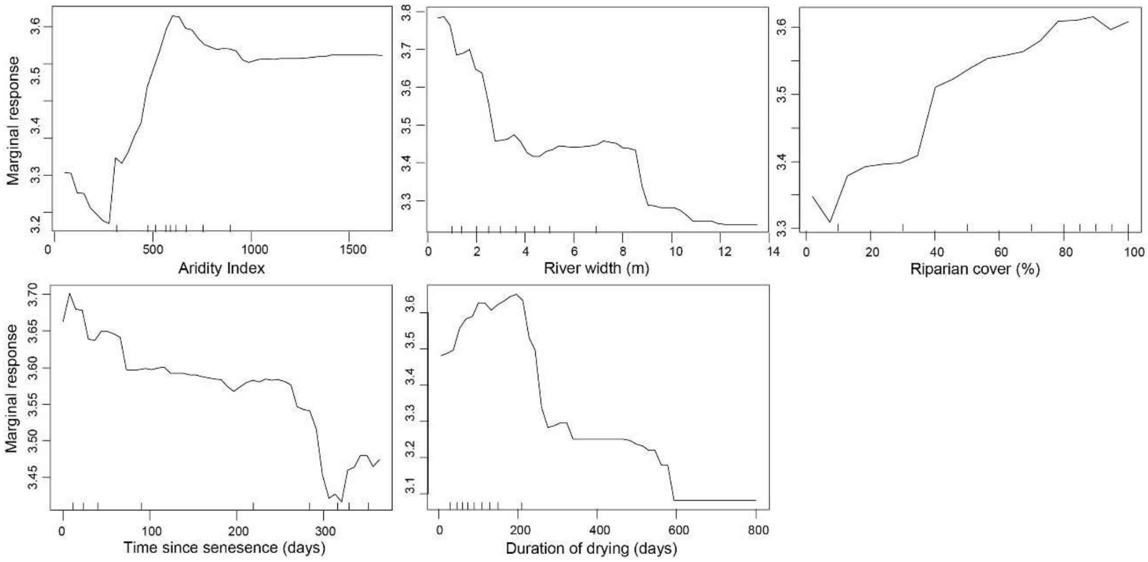

Figure 2. Partial dependence of the probability of the quantity of LL accumulated on dry riverbeds for the main predictors of random forest models. Variables are shown from the top left to the bottom right in order of decreasing importance. The plots show the marginal contribution to probability of the quantity of LL accumulated in dry reaches (marginal response, y-axis) as a function of the predictors (i.e. when the other contributing predictors are held at their mean). The rug plots on the horizontal axes show deciles of the predictors.

Decomposability of accumulated leaf litter

The C:N ratio of LL, as a first proxy of decomposability, ranged from 17 to 154 (mean ± S.D. = 46 ± 23) and was driven by climate, riparian cover, and dry period duration, as predicted by our conceptual model (Fig. 1). However, the RF model explained only 14.9% of the total variance in C:N (Table 2). The relationship of the C:N ratio with mean annual potential evapotranspiration (PET) was not monotonic in that the C:N ratio increased sharply between about 700 and 900 mm PET year^{-1} and then gradually decreased. The C:N ratio decreased with riparian cover and the aridity index, the latter relationship resembling the reverse of its response to dry period duration. Aridity was an important influence on C:N, with lower ratios reported for low-aridity environments, including tropical conditions, compared to other climate types (Aerts 1997; Boyero et al., 2017). More research is needed to determine how plant species richness, vegetation structure and functional diversity in riparian zones affect the C:N and decomposability of LL in dry riverbeds.

Decomposability was also related to preconditioning after LL deposition on dry riverbeds. A few days of drying on the riverbed decreased the C:N ratio of LL, whereas longer drying periods resulted in increases, with peaks occurring after ~100 days before C:N declined again, levelling off after 200 days. The increase in C:N with dry period duration suggests that nutrients, along with other soluble compounds, are preferentially leached from LL in dry riverbeds, resulting in litter composed mostly of nutrient-poor structural compounds such as cellulose and lignin (Cleveland et al., 2004). The initial decomposability of LL falling onto dry riverbeds and subsequent quality changes affect decomposition in both the receiving and downstream reaches (Corti & Datry 2012). Thus, climate change-related extensions of dry periods (Jaeger et al., 2014) could increase downstream transport of low-quality LL, with potential repercussions on detrital food webs and associated ecosystem functions and services.

Respiration and potential CO_2 release after leaf litter rewetting

We did not determine decomposition rates directly, but used a proxy of terrestrial litter decomposability by measuring oxygen consumption related to rewetting in laboratory conditions. Oxygen consumption rates of rewetted LL ranged from 0.004 to 0.97 mg O_2 g^{-1} dry mass h^{-1} (mean $\pm$ S.D. = 0.36 $\pm$ 0.20, median = 0.29). These values are in the upper range of respiration rates reported from coarse-particulate organic matter in fresh waters and soils (0.009-0.55 and <0.001–0.35 mg O_2 g^{-1} dry mass h^{-1} for fresh waters and soils, respectively). This indicates that rewetting events are associated with intense biological activity, when the highly labile C fuelling the initial respiration after rewetting can be rapidly metabolised by most heterotrophic microorganisms present in the litter (Foulquier et al., 2015). The global RF model explained 36.8% of the total variation in O_2 consumption rates, with the most important predictors being the riparian forest proportion in the catchment, catchment area, the time since senescence, dry period duration, aridity, and the C:N ratio (Table 2). Rates increased with catchment area, and decreased with forest proportion, aridity, C:N, time since senescence, and dry period duration. Upon flow resumption, higher microbial respiration rates are triggered when previous drying events are short compared to extended dry phases. The predicted increase in the frequency of drying events (Larned et al., 2010; Jaeger et al., 2014) might thus have strong implications on IRES metabolism and increase their contribution to the global C cycle through CO_2 emissions upon rewetting.

Our estimates of CO_2 emissions from IRES upon LL rewetting ranged from 0 to 13.7 g CO_2 m^{-2} day^{-1} (mean $\pm$ S.D. = 0.88 $\pm$ 1.51, median = 0.42), which is in the upper range of previously reported emission rates from fresh waters and soils. Notably, the highest values are 10 fold higher than those reported in the most comprehensive estimates of CO_2 emission rates available from inland waters (Raymond et al., 2013), in which reservoirs are expected to release up to 0.34 mg CO_2 m^{-2} day^{-1} and perennial streams up to 1.75 mg CO_2 m^{-2} day^{-1}. Our highest potential short-term CO_2 emission rate associated with litter rewetting could thus represent up to 152% of previous estimates from perennial streams and rivers (min = 0%, mean = 3-10%, max = 47-152%. This is remarkable, especially since our estimates are conservative, because they are mainly based on microbial activity on LL and exclude sediment respiration. The highest emission rates were found at sites characterized neither by the highest O_2 consumption rates nor by the highest quantities of accumulated LL, indicating that the two variables are uncorrelated. This highlights the need to consider both LL quantity and decomposability, to evaluate the role of IRES in the global C cycle.

The RF model explained 34.9% of the total variation in the potential CO_2 released and estimated time since senescence, aridity, and drying duration as the most important predictors (Table 2, Fig. 3a). Relationships were typically non-monotonic. The CO_2 released decreased sharply until 85 days after estimated senescence, before remaining relatively low and stable (Fig. 3a). CO_2 release decreased till an aridity index value of 230, then increased sharply till 700 to decrease again and stabilise at values above 800 (Fig. 3a). Last, rates of CO_2 release remained stable for 200 d of dry riverbeds, but sharply decreased thereafter (Fig. 3a). Although IRES release CO_2 during both flowing (Raymond et al., 2013; Hasler et al., 2016) and dry (Gómez-Gener et al., 2016) phases, our study suggests that early stages of rewetting can be considered hot moments (Larned et al., 2010; Datry et al., 2014) or control points (Bernhardt et al., 2017) of CO_2 release. This finding is important because global estimates of CO_2 release focusing on perennial rivers (Raymond et al., 2013; Hotchkiss et al., 2015; Butman et al., 2016) have missed emissions from at least 84,000 km^2 of river channels by overlooking IRES (Benstead & Leigh 2012; Raymond et al., 2013).

Differences among climate zones

Our global study demonstrates that the quantities of organic material accumulating during dry phases in riverbeds vary substantially among climate zones. Temperate IRES accumulated more LL (mean $\pm$ S.D. = 97 $\pm$ 152, median = 41 g dry mass m^{-2}) than those in the tropics (mean $\pm$ S.D. = 32 $\pm$ 44, median = 9 g dry mass m^{-2}) and arid climates (mean $\pm$ S.D. = 45 $\pm$ 64, median = 7 g dry mass m^{-2}) (ANOVA, $P < 0.001$). Of the sampled riverbeds, 150, 31, 19, and 10 were located in temperate, arid, tropical and continental climates, respectively, reflecting the geographical spread of current IRES research (Leigh et al., 2016) and highlighting that our results need to be interpreted with caution in less well-represented climate classes, particularly in alpine (only a single location), continental and, to a lesser extent, tropical IRES. When ran separately for different climate zones, RF model performance to predict the quantity of accumulated LL was indeed much higher for temperate and arid (36.1% and 26.8% of total variance explained, respectively) than for tropical (5.6%) climates. Thus, our conclusions are more solid in temperate and arid climates, where IRE are widespread, compared to the tropics (Stubbington et al., 2017; Datry et al., 2017). For example, IRES represent up to 45% of the hydrological network in temperate France (Snelder et al., 2013) and up to 96% in the arid south-western U.S.A (Tooth 2000; Levick et al., 2008). Tropical IRES often have higher annual LL inputs than temperate forests (Huston & Wolverton 2009), but our ability to predict their LL accumulation in these riverbeds was reduced, probably because of often continuous leaf fall (Murphy & Lugo 1986). This result might indicate that C cycling in IRES is less punctuated in tropical than in other climates, although identical predictors were retained by the respective RF models, indicating that litter accumulation is controlled by common factors across all climatic zones.

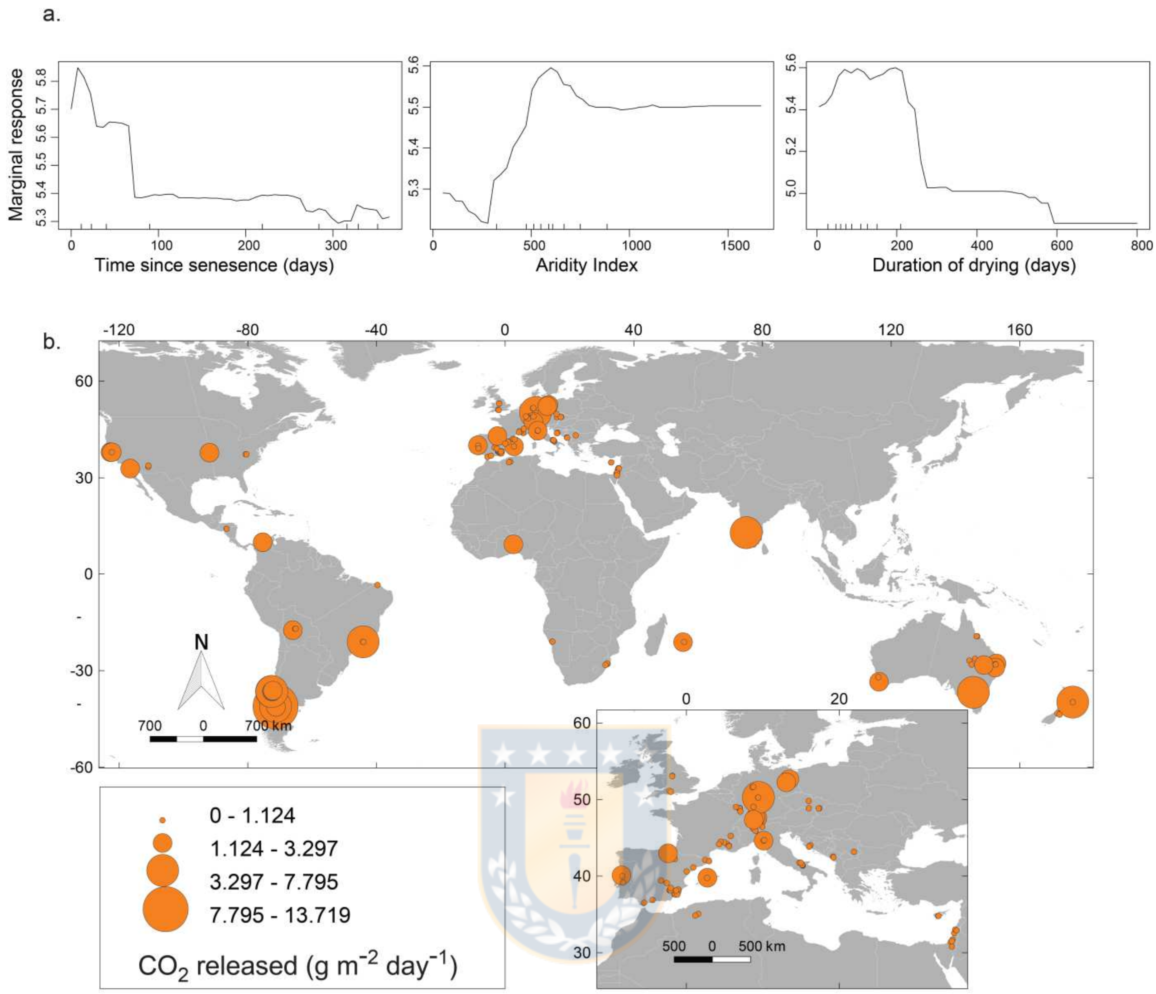

Figure 3. a. Partial dependence of the probability of the CO_2 released by rewetted LL over 24 h for the main predictors of random forest models. Variables are shown from left to right in order of decreasing importance. The plots show the marginal contribution to probability of the CO_2 released by rewetted LL over 24 h (marginal response, y-axis) as a function of the predictors (i.e. when the other contributing predictors are held at their mean). The rug plots on the horizontal axes show deciles of the predictors. b. CO_2 released mapped onto the original sampling reaches.

Our findings on LL accumulation were paralleled by estimates of CO_2 release upon rewetting, which were also much higher in temperate (mean $\pm$ S.D. = 1.06 $\pm$ 1.76 g CO_2 m^{-2}) than in arid and tropical IRES (0.48 $\pm$ 0.68 and 0.28 $\pm$ 0.35 g CO_2 m^{-2}, respectively). However, this comparison is influenced by the limited ability of our models to predict CO_2 release from arid IRES (4.4% of the variance explained) compared to temperate and tropical IRES (33.5 and 16.8% of the variance explained, respectively). This may reflect the importance of abiotic processes such as photodegradation for LL decomposition in water-limited river ecosystems (Austin & Vivanco 2006) or the influence of plant functional traits, not included in our model, that are involved in the protection from desiccation and solar radiation, such as the quantity of waxes and phenolic compounds (De Deyn et al., 2008).

Discussion

Implications and perspectives

Our global approach involving more than 200 sites on all continents (i) enabled us to document the extent of global variation in TPL and LL quantity and quality across dry riverbeds, and (ii) revealed high O_2 consumption and CO_2 release rates after LL rewetting, notably in temperate regions. These findings support the notion of IRES as punctuated biogeochemical reactors (Larned et al., 2010), characterized by distinct phases of C accumulation and processing with much higher temporal variability in process rates than in perennial river ecosystems.

Transport distance and site of litter deposition and processing after flow resumes will vary with river morphology and the magnitude of the flow pulse (Corti & Datry 2012). However, except during extreme flow conditions, much of the mobilised litter will remain in river channels and riparian areas, where it decomposes at rates similar to those in perennial rivers.

Since these rates are much faster than in upland terrestrial sites (Boyero et al., 2012; Foulquier et al., 2015), these findings suggest that neglecting IRES leads to a notable underestimation of the contribution of the world's river network to the total global CO_2 flux to the atmosphere. Our study suggests that in addition to globally relevant amounts of CO_2 released from IRES during both dry (Gómez-Gener et al., 2016) and flowing phases, rewetting events act as hot moments (Larned et al., 2010) or control points (Bernhardt et al., 2017). This would imply upward revision of organic matter transformations and CO_2 emissions from river networks on the global scale, since IRES could increase annual estimates of global CO_2 emissions from streams and rivers by 7-152%, the CO_2 released from LL during a single rewetting event alone contributing from 3 to 10% of this increase. Likewise, taking IRES into account would improve estimates of the consequences of global climate change on C cycling, since IRES are predicted to expand in both time and space (Larned et al., 2010; Datry et al., 2014; Jaeger et al., 2014).

The data and conceptual framework presented here provide the basis needed to develop models of litter decomposition and C cycling in fresh waters that include IRES. The next steps would be to quantify CO_2 emissions upon flow resumption *in situ* (Corti & Datry 2012) and collect data on LL quantity and decomposability for continental and other climates that are not well represented at present. CO_2 emissions from dry (Gómez-Gener et al., 2016) and flowing (Raymond et al., 2013; Hasler et al., 2016) phases then need to be integrated with those during wetting events, and temporal variability (including its dependency on other environmental conditions, such as temperature) be studied for extended periods after flow resumes to build adequate quantitative models of global C cycling that consider the spatio-temporal dynamism of IRES under present and future climatic conditions.

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CAPÍTULO III: Dinámica de nutrientes en agua superficial e hyporheo durante la rehumectación de un río intermitente de Chile Mediterráneo

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Articulo en revisión

Contribución de los autores

Kate Brintrup y Ricardo Figueroa contribuyeron con el diseño y concepción del estudio. Las muestras, su posterior análisis y procesamiento fue realizado por kate Brintrup. Katia Sáez, Pablo Pedreros apoyaron los análisis estadísticosEl primer manuscrito fue hecho por Kate Brintrup y fue revisado por Ricardo Figueroa, Mariela Yevenes, y Andrea Butturini. Todos los autores han leído y aprobado el manuscrito final.

Resumen

Los ríos intermitentes y arroyos efímeros (IRES) están presentes en todo el mundo y predominan en regiones de clima mediterráneo, las más sensibles al cambio climático y modificaciones del uso de suelo. En estos ríos la variabilidad del régimen hídrico genera una dinámica particular de nutrientes, donde la zona hyporheic (HZ) juega un papel fundamental en los procesos biogeoquímicos. El objetivo de este estudio fue evaluar si después de un periodo de sequía el primer pulso de inundación que genera la reconexión del flujo afecta las concentraciones de nitrógeno inorgánico disuelto (DIN), nitrógeno total (TN), fósforo total (TP), sólidos suspendidos (SS), sólidos disueltos (DS), así como variaciones en pH, conductividad, oxígeno disuelto (DO), temperatura (T) del agua superficial, nitrógeno inorgánico disuelto (DIN) en agua superficial y HZ, en dos tramos del río Lonquén; Rincomávida (RM) y Buenos Aires (BA), Chile mediterráneo, para los años 2015 y 2016. En ambos años no se detectó un patrón entre fragmentación y reconexión. Así mismo, no se observan condiciones de anoxia, lo que ocasiona que muchas de las variables no tengan diferencias significativas luego de la reconexión, especialmente conductividad, DIN de agua superficial y HZ. pH disminuyó significativamente ($p<0.05$) en el año 2016. DS tuvo el valor más alto durante la reconexión del año 2016 en BA (177.8 mg L^{-1}). SS solo tuvo cambios significativos en el año 2015 con tendencia al incremento en RM (48.57 mg L^{-1}). TP incrementó en ambos tramos el año 2015, en cambio TN disminuyó significativamente ($p<0.05$) en casi todos los sitios y años, su mayor concentración fue en fragmentación de BA el año 2015 (2.01 mg L^{-1}). La reconexión del río puede afectar las concentraciones de algunas variables, debido a la susceptibilidad del

sistema a las condiciones de humedad del suelo, lluvias precedentes y régimen hidrológico, sin embargo, N pueden ser procesado rápidamente por las bacterias del hiporreo.

Palabras clave: río intermitente, hiporreo, procesos biogeoquímicos, pulso de inundación y clima mediterráneo.

Introducción

En climas mediterráneos, los ríos intermitentes son el tipo dominante y podrían incrementar alrededor del mundo como consecuencia del calentamiento global y los cambios de uso del suelo que modifican el régimen hidrológico (Gasith y Resh., 1999; Tockner y Stanford, 2002; Gleick 2003; Larned et al., 2010; Acuña et al., 2014; Jaeger et al., 2014). Estos ecosistemas se caracterizan por tener un ciclo hidrológico anual altamente variable, con fases de desecación, contracción, fragmentación y reconexión del flujo (Froebrich, 2005; Lillebo et al., 2007, von Schiller et al., 2011). Estos cambios influyen directamente en la conectividad hidrológica del río determinando las tasas de procesamiento de nutrientes y distribución espacial de organismos que participan en el proceso de desecación (Dent y Grimm 1999; Motta et al., 2017).

La principal entrada de nutrientes a los sistemas fluviales viene desde fuentes alóctonas, por escorrentía superficial, de la vegetación ripariana y de fuentes difusas que participan en procesos internos de mineralización biogeoquímica (Dahm et al., 2003; Acuña et al., 2005; von Schiller et al., 2011). Estos procesos internos son más intensos durante los periodos de sequía (Capone y Kiene, 1998), donde la alta temperatura del agua y la escasa concentración de oxígeno favorece la amonificación, proceso que reduce los compuestos orgánicos que contienen nitrógeno, por ejemplo la urea y ácido úrico, liberando como producto el amonio (Lillebo et al., 2007; von Schiller et al., 2011; Katipoglu et al., 2012), por lo tanto, se incrementan las concentraciones de amonio y otras formas reducidas de nutrientes inorgánicas, en los primeros centímetros de sedimento (Vidal-Abarca et al., 2000; Acuña et al., 2005; Lillebo et al., 2007), posteriormente, la rehumectación y expansión del sistema acuático trae como consecuencia altos niveles de fósforo (P), nitrógeno (N) y SS, provenientes del flujo subterráneo y procesamiento de materia orgánica acumulada en el lecho del río. Estas áreas ricas en nutrientes se movilizan con los primeros pulsos de inundación (Tzoraki et al., 2007; Obermann et al., 2009; Shumilova et al., 2019). Mientras es transportado, el P puede sufrir captación/liberación, adsorción/desorción, precipitación/disolución o advección/difusión (Vannote et al., 1980; Bryce et al., 1999; Withers y Jarvie 2008; Steward et al., 2012). En los ríos intermitentes los procesamientos de nutrientes son además dependientes de las distintas fases de contracción, fragmentación y rehumectación que favorece la dinámica temporal y espacial de nutrientes (Boulton y Lake 1990; Stanley et al., 1997; Dent y Grimm, 1999; Baldwin et al., 2005; Arce et al., 2014), por ejemplo, durante la sequía, la mortalidad microbiana y la exposición prolongada del sedimento liberan grandes cantidades de N y P (Baldwin y Mitchell 2000; Amalfitano et al., 2008).

La zona hiporreica (HZ) es un ecotono activo entre el agua superficial y subterránea (Mulholland et al., 2000; Krause et al., 2009), aquí la hidrología, tiempo de residencia, humedad, entre otros factores, influirán sobre la absorción del carbono orgánico disuelto y la nitrificación, definida como la transformación biológica de formas reducidas de nitrógeno a nitrato (Boulton et al., 1998; Koops y Pommerening-Röser 2001). Por otro lado, el agua superficial aporta oxígeno y compuestos orgánicos a los microorganismos e invertebrados de la HZ, mientras que el agua subterránea suministra nutrientes a los organismos de la columna de agua (Boulton et al., 1998). De modo que la HZ puede también influir en la disminución de los niveles de nitrato (NO_3^-) en el agua superficial debido a los procesos de desnitrificación, ya que el NO_3^- es oxidado por microorganismos en condiciones anóxicas (Puckett et al., 2008; Krause et al., 2009). Por esta dinámica bastante estudiada (Boulton et al., 1998; Mulholland et al., 2000; Peterson et al., 2001; Puckett et al., 2008; Krause et al., 2009; Arce et al., 2014), se reconoce como una zona donde existen mecanismos de atenuación de nutrientes (Environment Agency, 2000; Smith, 2005), otorgándole una valoración intrínseca y ecosistémica a proteger, más aún cuando en los ríos intermitentes se acentúa este procesamiento de nutrientes por la adaptación que tiene la biota microbiana (Austin et al., 2004; Sponseller, 2007; Scherer et al. 1984; Vincent y Howard-Williams, 1986). Además en ríos intermitentes de Chile Mediterráneo, no se conocen estudios que respalden este rol depurador de aguas, tampoco se ha investigado la influencia de la intermitencia de flujo sobre los nutrientes. Bajo este escenario, nosotros hipotetizamos que en la reconexión del flujo existirá un incremento en las concentraciones de nutrientes en el agua superficial, y disminución en agua de hiporreo, para lo cual se estudió la dinámica de nutrientes en agua superficial e hiporreo en la fase de cese y reanudación de flujo durante dos años hidrológicos consecutivos en un río intermitente de Chile Centro-sur.

Metodología

Área de estudio

El río Lonquén, es un río predominantemente intermitente, con algunos tributarios perennes. Pertenece al secano costero de la Cordillera de la Costa en la zona centro sur de Chile Mediterráneo (36° 25' 59,88'' S; 72° 42' 0'' W) y presenta altas variaciones de precipitación y temperatura entre estaciones. La temperatura media anual es de 14.1°C y precipitación total anual de 897.9 mm (Duissaillant, 2009). Los periodos de contracción y fragmentación del flujo comienzan en diciembre con el cese del flujo y desarrollo de pozas aisladas, posteriormente la reconexión ocurre en junio-julio. Su cuenca tiene forma irregular (Figura 1), y drena un área de 1075 km^2. El uso del suelo está representado principalmente por plantaciones forestales (*Pinus radiata* y *Eucalyptus globulus*), viñedos y matorrales. La geomorfología se encuentra fuertemente meteorizada, de relieve envejecido, con rocas graníticas y pizarras metamórficas.

Hidrología y meteorología

Los datos de caudales y precipitaciones fueron extraídos de la base de datos de la Dirección General de Aguas de Chile (DGA), desde las estaciones fluviométricas y meteorológicas (08144001-8 y 08118004-0, respectivamente). El caudal base del río fluctúa entre 0 y 10 $m^3 s^{-1}$, y el caudal medio mensual es de 13.07 m^3s^{-1}. Su flujo es de tipo intermitente, con fuertes precipitaciones en invierno y sequías extremas en verano. Se determinó el índice de precipitación precedente (API) para modelar la relación lluvia-escorrentía y determinar la humedad del suelo previo a las tormentas que generan las reconexiones (Bruce y Clark, 1966; Fedora y Beschta, 1989; Perrone y Madramootoo, 1998), según:

$$API = k * P_1 + k^2 * P_2 + \ldots + k^n * P_n \quad (1),$$

Donde P_1, P_2,..., P_n es la precipitación, 1, 2,..., n son los días previos al evento y k es una constante derivada de análisis de recesión de múltiples hidrogramas de tormenta, proporcional al tamaño de la cuenca y generalmente es más bajo en el verano, en nuestro caso es 0.85. API clasifica tres condiciones de humedad precedente: condición 1; 0 ≤ API ≤ 15 mm (dry), condición 2; 15 ≤ API ≤ 30 mm (average) y condition 3; API > 30 mm (wet). Adicionalmente, se determinaron las siguientes variables; $Rain_1$, $Rain_2$, $Rain_3$ y $Rain_4$, que corresponde a la lluvia total durante el primer, segundo, tercer y cuarto mes antes de la reconexión (mm) y $Rain_{1-4}$: lluvia total en mm caída durante los cuatro meses antes de la reconexión.

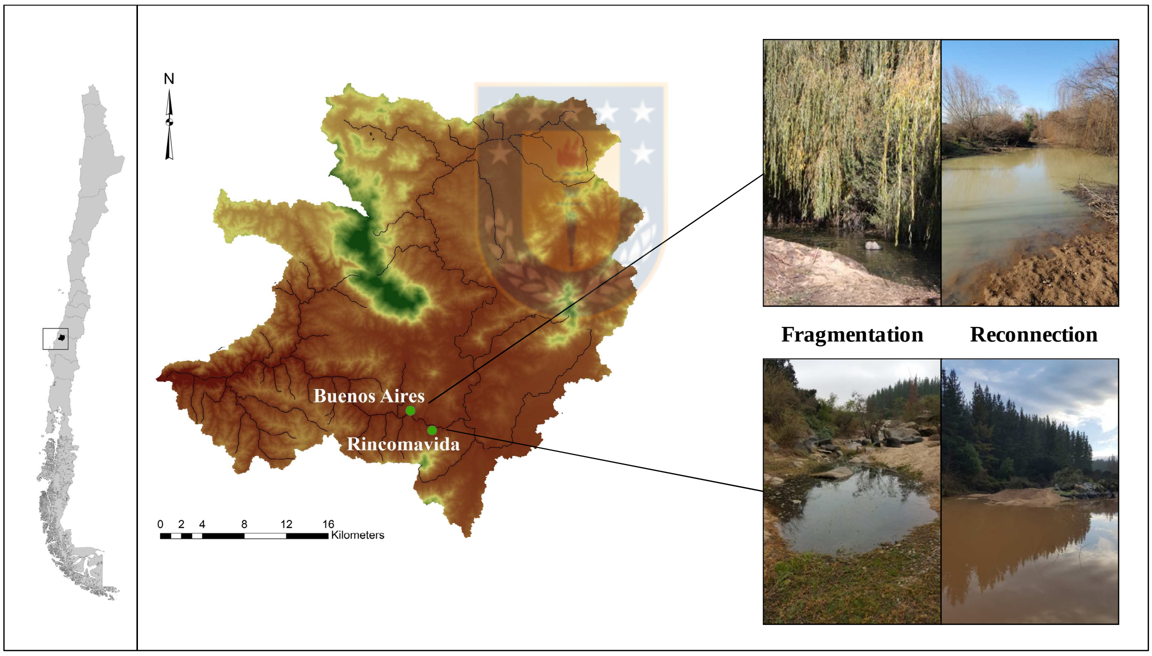

Figura 1. Localización de los tramos de muestreo Buenos aires (BA) y Rincomávida (RM) en el río Lonquén.

Variables físico-químicas

En dos tramos del río Lonquén (Buenos Aires y Rincomávida, Figura 1) se recolectaron muestras en las fases de fragmentación y reconexión del río durante dos años hidrológicos consecutivos (2015 y 2016). Se tomaron muestras de agua superficial en triplicado tres veces al día (10:00 AM; 14:00 PM y 18:00 PM) y para agua de HZ una vez al día. En el agua superficial se evaluó *in situ* conductividad, temperatura, oxígeno disuelto (DO) y pH mediante una sonda multiparamétrica (Hydrolab Quanta multiparameter). Además, se tomaron muestras para DIN, TP, SS, DS y TN. Las muestras para los iones nitrito (NO_2^-), NO_3^- y amonio (NH_4^+) fueron filtradas *in situ* (Durapore PVDF de 0.45 µm). Posteriormente los aniones (NO_2^- y NO_3^-) y cationes (NH_4^+) se analizaron en los cromatógrafos DIONEX ICS-2000 y DIONEX ICS-2100, respectivamente. DIN se calculó a partir de la adición de las concentraciones de N-NO_2^-, N-NO_3^- y N-NH_4^+. TP fue preservado *in situ* con 2 mL de ácido sulfúrico al 95-97% y analizado junto con TN en espectrofotómetro UV/VIS Lambda 25 de Perkin Elmir. El agua fue filtrada mediante un filtro de fibra de vidrio (GF/F de 0.45 µm) hasta un máximo de 2000 ml. Los SS retenidos en el filtro fueron secados en horno por 48 h a 60 °C y el líquido filtrado fue secado 48 h a 100 °C para DS.

Desde el agua del hyporheo se tomaron muestras para DIN mediante un testigo de sedimento a través de un muestreador de agua intersticial Rhizon Sampler (Seeber-Elverfeldt et al., 2005) a profundidades de 0.0, 0.5, 1.0, 1.5, 2.5, 3.5, 5.0, 7.5, 10.0, 12.5 y 15.0 cm., cuando esto fue posible.

Análisis de datos

Los resultados de las concentraciones de las variables se ajustaron a la mitad del límite de detección cuando los valores de los análisis químicos estuvieron bajo el límite de detección. Para explorar relación entre el caudal y la precipitación, se utilizó correlación de Spearman. La evaluación de las diferencias significativas entre los años 2015 y 2016, y los periodos de fragmentación/reconexión para las variables fisicoquímicas, se hizo mediante Kruskal-Wallis. Todos los análisis se realizaron mediante el software R versión 3.1.1.

Resultados

El análisis de correlación entre la precipitación y el caudal indica que estas variables están relacionados significativamente ($p<0.05$, Fig. 2) en ambos años. API indica un suelo en condiciones secas, sin embargo, en el primer año de estudio las condiciones hidrológicas previas a la reconexión fueron más húmedas que el segundo año. Las primeras precipitaciones ($Rain_1$) en el año 2015 fueron más fuertes y ocurrieron pocas semanas antes de la reconexión (Tabla 1). En ambos años el tiempo de duración de ausencia de flujo es mayor que la conectividad del sistema (Tabla 1).

Tabla 1. Variables hidrológicas durante el periodo de estudio en río Lonquén (API: Índice de precipitaciones precedentes a la reconexión del río; $Rain_1$, $Rain_2$, $Rain_3$ y $Rain_4$: lluvia total durante el primer, segundo, tercer y cuarto mes antes de la reconexión (mm); $Rain_{1-4}$: lluvia en mm total durante los cuatro meses antes de la reconexión).

Variables	2014-2015	2015-2016
Reconexión	10-jul-15	11-jul-16
Fragmentación	12-dic-15	11-nov-16
Días de fragmentación	240	213
Días de conexión	155	124
API	0.23	0.09
$Rain_1$	63.20	4.30
$Rain_2$	24.50	87.70
$Rain_3$	0.20	21.20
$Rain_4$	0.00	0.00
$Rain_{1-4}$	87.90	113.20

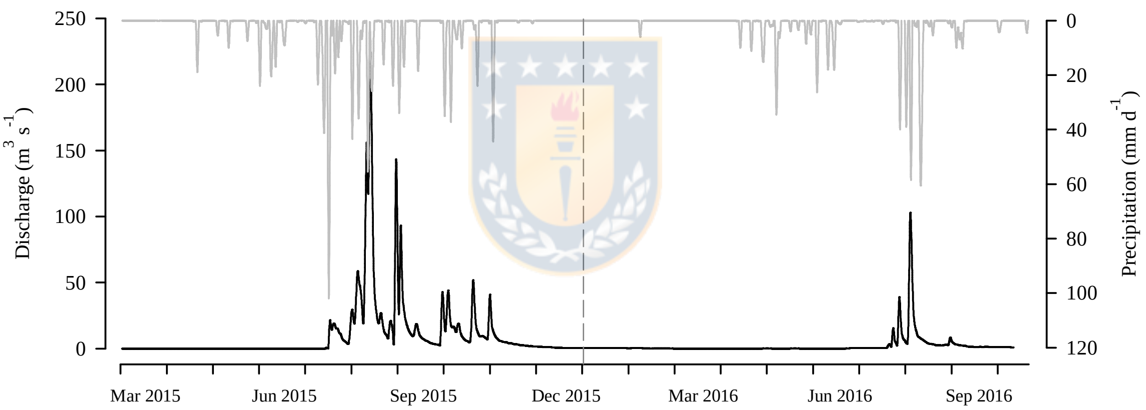

Figure 2. Daily mean discharge (black) and daily precipitation (grey), during the study period in Lonquén river, Chile.

Las variables fisicoquímicas en ambos años son estadísticamente diferentes ($p<0.05$), por lo tanto, se consideran los dos años de muestreo de forma independiente.

Respecto de las variables en relación a la transición entre las fases fragmentación y posterior reconexión (figura 3), DO y conductividad casi no evidencian cambios, y temperatura disminuye en todos los casos. pH no varía en el año 2015, mientras que disminuye en ambos tramos en el año 2016. DS incrementa significativamente en el tramo BA en ambos años. La concentración de SS incrementa significativamente en el tramo Rincomávida, durante el año 2015, en los otros periodos, también existe un incremento pero no es significativo. TP incrementa significativamente en ambos tramos solo en el año 2015, al año siguiente no hay cambios significativos. TN cambia significativamente en todos los casos, en el año 2015 disminuye en ambos tramos, mientras que al año siguiente, incrementa en BA y disminuye en RM. DIN no tiene cambios significativos en todo el periodo de estudio y en hyporheo esta variable disminuye significativamente en el tramo RM el primer año, y el segundo año incrementa en BA (figura 3).

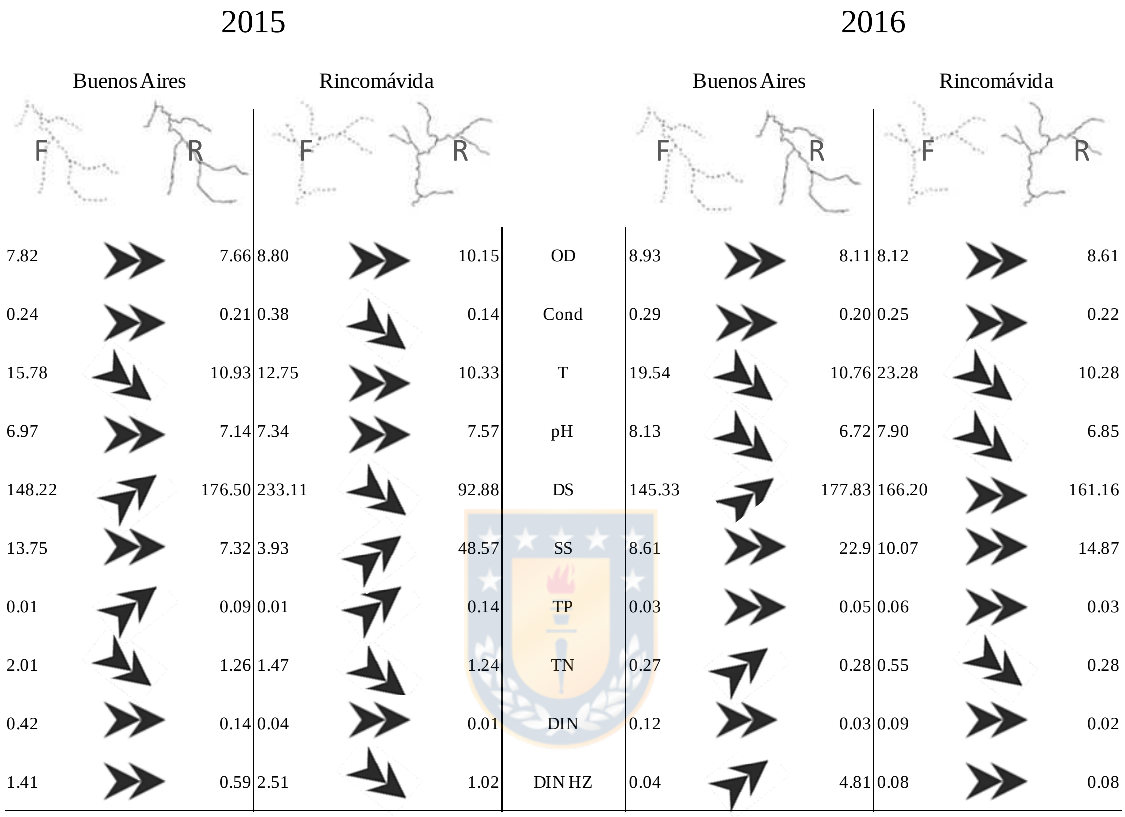

Figura 3. Dinámica temporal de variables durante las fases hidrológicas de fragmentación (F) y reconexión (R) en los tramos Buenos Aires y Rincomávida en la cuenca del río Lonquén. Las variables son: OD; oxígeno disuelto (mg L^{-1}), Cond; conductivity (mS cm^{-1}), T; temperature (°C), pH, DS; sólidos disueltos (mg L^{-1}), SS sólidos suspendidos (mg L^{-1}), TP; fósforo total (mg L^{-1}), TN; nitrógeno total (mg L^{-1}), DIN; nitrógeno inorgánico disuelto (mg L^{-1}) y DIN HZ; nitrógeno inorgánico disuelto en zona de hyporheo (mg L^{-1}). Flecha con dirección ascendente indica un incremento significativo ($p<0.05$) luego de la reconexión, flecha con dirección descendente indica lo contrario. No hay cambios significativos si la flecha está en dirección horizontal.

Discusión

La disminución del flujo en el río intermitente Lonquén reduce la cantidad de materia orgánica, sedimentos y nutrientes transportados, aumentando el tiempo de residencia (Dahm et al., 2003; Harvey et al., 2003) y el procesamiento de esta materia orgánica y nutrientes en el agua superficial, zonas parafluviales e hyporheo (Harvey et al., 2003; Dent y Grimm, 1999). Además se incrementa la retención de nutrientes desde la zona ribereña (Bernal y Sabater, 2012). El cese de flujo genera una consecuente fragmentación del sistema, formando un conjunto de pozas aisladas (Stanley et al., 1997). Generalmente en estado de fragmentación predominan los procesos anaeróbicos, debido a la acumulación y procesamiento de materia orgánica, elevadas tasas de respiración y baja renovación del agua (Boulton y Lake, 1990; Acuña et al., 2005; Lillebo et al., 2007; von Schiller et al., 2011).

En estas condiciones hipóxicas, en la mayoría de los ríos intermitentes, el nitrato disminuye debido a la desnitrificación y el amonio incrementa por la mineralización de las hojas que se acumulan en las pozas (Pinay et al., 1994; Acuña et al., 2005; von Schiller et al., 2011), fotodegradación de la materia orgánica en el sedimento seco (Larson et al., 2007), también por la transformación del nitrato en amonio con bajo potencial redox (Arce et al., 2014), desorción de sedimentos, inhibición de la nitrificación (Baldwin y Mitchell, 2000), rompimiento celular de biofilm (Humphries y Baldwin, 2000) y evaporación (McLaughlin, 2008). También el P puede incrementar en condiciones anaeróbicas, debido a su liberación desde el sedimento a la columna de agua (Baldwin et al., 2000; Lillebo et al., 2007), además gran cantidad de P puede estar en forma particulada (Skoulikidis y Amaxidis, 2009) y biodisponible, debido al previo secado del sedimento, en la fase seca (Kerr et al., 2010). Durante el primer pulso de inundación, el DIN y P acumulado en el agua del poro de sedimento y pozas es resuspendido y liberado a la columna de agua y hacia el agua subterránea (Butturini et al., 2003). Según Arce et al. (2014), el sedimento de ríos intermitentes podría ser una fuente importante de nitrógeno, y potencialmente podría liberar hasta 6 veces más NO_3^- en la columna de agua post rehumectación en relación a un tramo perenne de características similares.

Es de esperar que esta alta carga de NO_3^- en la columna de agua sea rápidamente abatida por las bacterias que se encuentran en HZ, ya que esta zona es el compartimento biogeoquímico más dinámico en el río (Dahm et al., 2003; Daesslé et al., 2017), donde existen microorganismos altamente adaptados al estrés hídrico (Fierer y Schimel 2002; Fierer et al., 2003), a las características del sedimento y sitio de estudio (Krause et al., 2009). Incluso los ríos urbanos degradados conservan la capacidad de transformar el nitrógeno y exhibir las funciones remanentes de los ecosistemas (Mayer et al., 2010), a través de la biota contenida en HZ. Estos procesos logran reducir las cargas de N liberadas al agua superficial y podrían explicar la escasa variabilidad de DIN en agua superficial e hiporreo en las fases de fragmentación y reconexión en el río Lonquén en el tramo BA en el año 2015 y RM en el año 2016. Sin embargo, las variaciones de DIN en hiporreo luego de la reconexión en el tramo RM en el año 2015 y BA en el año 2016 podría deberse a la metodología empleada, ya que el core se toma en un punto de la poza, y tras la reconexión es muy difícil coincidir en la misma área, por otro lado, los ríos intermitentes, especialmente en estado fragmentado y bajo caudal, son considerados reactores biogeoquímicos puntuales (Larned et al., 2010), por lo tanto en un tramo, los procesos pueden diferir substancialmente.

En el río Lonquén no se registraron condiciones de hipoxia, esto puede ser reflejo de la actividad fotosintética asociada a la comunidad de microalgas, gran tamaño y profundidad de las pozas (Dahm et al., 2003). También se encontró una mayor conductividad en las pozas que en reconexión, similar a lo encontrado por Acuña et al. (2005). Dadas estas condiciones ambientales, los niveles de nitrógeno, como DIN y TN se mantienen e incluso son más altos en las pozas que en la reconexión, y el peak de la concentración de P durante la reconexión del flujo en el río Lonquén, es más bajo que el N, esto se explicaría por la alta cantidad de N liberada desde el sedimento y suelos, además de dilución de P (Tzoraki et al., 2007; von Schiller et al., 2011; Baldwin et al., 2000). Sin embargo, a diferencia de von Schiller et al. (2011), durante la reconexión del flujo en el año 2015, la concentración de TP fue alta. Esta condición podría atribuirse a la asociación de P con sólidos en suspensión, debido a una previa mineralización del detrito acumulado en el sedimento (Acuña et al., 2005), a un bajo procesamiento del fósforo, dada la alta velocidad de la corriente e ingreso de agua proveniente de la escorrentía superficial (Fazi et al., 2008), mayor ingreso del agua subterránea y oxígeno, reducción del desarrollo autotrófico, pH cercano a neutro (Dahm et al., 2003), fenómeno muy distinto a lo reportado por Baldwin et al. (2000).

La alta concentración de SS durante la reconexión del flujo en el año 2015 en RM coincide con Obermann et al. (2009), además Skoulikidis y Amaxidis (2009) también encontró un aumento significativo de SS y nutrientes asociados a la intensa erosión de la cuenca, aunque en el Lonquén este aumento no es significativo en otros sitios y periodos.

En el área de estudio, no fue posible encontrar un patrón en todos los sitios y años, por otro lado no necesariamente se cumplen los cambios biogeoquímicos descritos por otros autores (Towns 1985; Stanley et al. 1997; Caruso 2002; Acuña et al., 2005; Lillebo et al., 2007), dado que las condiciones ambientales, precipitaciones y humedad del suelo (índice API) previo a la reconexión del río varían en cada caso, según (Holmes et al., 1998; Acuña et al., 2004) generando alta heterogeneidad espacial y temporal de las variables biogeoquímicas estudiadas. Posiblemente estos resultados se ven afectados aún más por la cantidad de muestras previo a la reconexión, por lo tanto, se recomienda realizar campañas más frecuentes desde el comienzo de la desecación, con réplicas de hiporreo y agua superficial en cada tramo para obtener una base de datos y análisis más robustos (Acuña et al., 2005; von Schiller et al., 2011).

Conclusión

La dinámica de nutrientes en el río Lonquén no muestra un patrón en el tiempo, ni entre los sitios, más bien responde a la teoría de reactor biogeoquímico puntual, dependiente de los procesos a nivel local, y también de las condiciones meteorológicas que afectan directamente la hidrología y por lo tanto a estos reactores. Se observa que precipitaciones menos intensas que se prolongan por más tiempo previo a la reconexión, favorecen la recarga de acuíferos subterráneos que interactúan con el río, determinando también el funcionamiento del hiporreo, que cumple un rol preponderante en las transformaciones biogeoquímicas, influyendo sobre el procesamiento de los nutrientes.

Con el cambio climático podrían incrementar los periodos de sequía en los ríos intermitentes, disminuir el nivel freático y el tamaño de las pozas, por lo tanto, se volverán anóxicas, favoreciendo procesos biogeoquímicos similares a los descritos en el Mediterráneo Europeo, como desnitrificación, amonificación y liberación de P desde el sedimento. Junto con la extensión de los periodos de sequía, se pronostican eventos de lluvia extremos, ambos escenarios afectarán la resiliencia de la microbiota del sedimento, reduciendo la capacidad de depuración de nutrientes.

Dado que el número y extensión de los ríos intermitentes incrementará en todo el mundo, se hace aún más relevante el estudio de la implicancia meteorológica e hidrológica sobre los procesos biogeoquímicos que se mantienen en el agua superficial e hiporreo, a través de muestreos continuos en las fases de desecación y primer pulso de inundación.

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CAPÍTULO IV: Biogeochemical dynamics during storm events in an intermittent mediterranean river in Chile

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Author's contributions

All the authors contributed to the conception and design of the study. The preparation of material, compilation of data and analysis were carried out by Kate Brintrup, Katia Sáez and Ricardo Figueroa. The first draft of the manuscript was written by Kate Brintrup and all the authors commented on previous versions of the manuscript. All the authors read and approved the final manuscript.

Conflicts of interest

The authors declare that there are no conflicts of interest.

Ethics approval

This article contains no study with human or animal participants carried out by any of the authors.

Abstract

Organic matter and nutrients in rivers can substantially increase during rain events causing eutrophication and hypoxia which can be more significant in intermittent rivers, where hydrological conditions are more extreme. The objective of this study was to determine the influence of streamflow on the variables dissolved inorganic nitrogen (DIN), total nitrogen (TN), total phosphorus (TP), suspended solids (SS), dissolved solids (DS), dissolved organic carbon (DOC) and properties of dissolved organic matter (DOM) in an intermittent river (Lonquén) of the Chilean mediterranean zone. Water samples were collected during three rain events and relationships between streamflows and the analyzed variables were determined through modeling, hysteresis and correlation; in addition, the loads of these variables were calculated for each event. In the first year, the variables

presented a counterclockwise pattern (flushing), except for DIN, which presented dilution, as did all the variables in the second event. The increase in the DOC concentration is related to greater aromaticity and molecular size and smaller molecular weight of DOM and a decrease in autochthonous DOM. The maximum DIN, TN, DS and DOC loads were recorded in the first rain event (9.6, 18.3, 2434.5 and 49.5 tons, respectively). In addition, a strong relationship between streamflow and DIN, TN, TP, DOC and DOM properties was observed in the last rain events; thus, streamflow could be a predictor of the biogeochemical dynamics in the surface water of the river.

Keywords: Intermittent river, storm, nutrients, dissolved organic matter, hysteresis.

Introduction

Intermittent rivers are important worldwide and it is estimated that they make up more than 50% of the global river network (Larned et al. 2010; Shumilova et al. 2019), a percentage that could increase in places experiencing drought due to climate change and greater water demand for socioeconomic uses (Larned et al. 2010).

DOM and nutrients are fundamental elements in continental aquatic systems for critical cellular processes of the biota and an increase in these solutes associated with rain events increases photosynthetic productivity and heterotrophic bacteria, leading to changes in food chains (Wetzel 1992; Buffam et al. 2001; Peterson et al. 2001; Ensign and Doyle 2006). However, these biogeochemical processes could be even more dynamic in intermittent rivers that are adapted to extreme hydrological conditions (Larned et al. 2010; Datry et al. 2014). During rain events, both DOM and nutrients are exported from streams and their drainage basins to higher-order rivers or coastal areas, where the quality of these elements regulates the metabolism of aquatic ecosystems (Meybeck 1982, 1993; Glibert et al. 2001; Cole et al. 2007; Paerl 2009; Yang et al. 2009; Welter et al. 2016). Information on DOM quality obtained through spectroscopy (fluorescence and absorbance) allows its allochthonous or autochthonous origin (Parlanti et al. 2000; McKnight et al. 2001; Huguet et al. 2009; Wilson and Xenopoulos 2009), degree of humification (Chen et al. 1977; Zsolnay et al. 1999), aromaticity (Weishaar et al. 2003) and molecular weight and size (De Haan and De Boer 1987; Helms et al. 2008), among other characteristics, to be discovered (Chen et al. 2003; McDonald et al. 2004). Some authors have determined that streamflow influences organic matter quality; for example, at low flows autochthonous DOM transport predominates, while at high flows DOM is aromatic and has greater molecular weight (Duan et al. 2007; Fellman et al. 2009; Pellerin et al. 2012; Fasching et al. 2016; Guarch-Rivot and Butturini 2016; Raymond et al. 2016).

Meanwhile, SS and DS can transport nutrients such as phosphorous and nitrogen and increase sedimentation rates on the riverbed, causing degradation and/or alteration of the aquatic habitat (Valero-Garcés et al. 1999; Oeurng et al. 2011; Cerro et al. 2013; Ramos et al. 2015), including processes of eutrophication and hypoxia in reservoirs, lakes or coastal systems (Datry et al. 2014), and can transport pesticide residues and trace heavy metals, among other substances (Herrera et al. 2013). Therefore, it is important to define input variations in terms of seasons and rainfall event magnitude, as hydrology and previous climate conditions are key in DOM, nutrient and solid dynamics (House and

Warwick 1998; Rovira and Batalla 2006; Butturini et al. 2008; Du et al. 2014; Fasching et al. 2016; Guarch-Ribot and Butturini 2016). In this regard, increased streamflow associated with a storm event can transport large quantities of solutes (Bowes et al. 2009, 2011; Oeurng et al. 2011; Gao et al. 2012; Roach 2013; Raymond et al. 2016; Lloyd et al. 2016), for example, reaching up to 75% of annual nitrogen export in some rivers (Bernal et al. 2005); specifically, it has been demonstrated that nitrate export predominates (Oeurng et al. 2010).

Most solute transport occurs during rainfall events, and the variation in DOC, nutrient and solid concentrations is often highly related to streamflow (Butturini 2008; Ward et al. 2012; Cerro et al. 2013; Du et al. 2014; Ramos et al. 2015; Bowes et al. 2015; Edokpa et al. 2015; Fasching et al. 2016; Lloyd et al. 2016), although it has been observed that DIN is not necessarily associated with streamflow (Oeurng et al. 2010; Cerro et al. 2013; Du et al. 2014; Ramos et al. 2015).

Nutrient, solid and DOM quality dynamics during rainfall events are little understood, especially in mediterranean climates; therefore, it is necessary to study biogeochemistry and its relationship with hydrology and the processes that direct patterns in organic matter and nutrient input into the system (Butturini et al. 2008; Ramos et al. 2015; Guarch-Rivot and Butturini 2016). In this context, the objective of this study was to analyze the influence of streamflow during rainfall events on nutrient, SS and DOM quality dynamics and their export in an intermittent river in mediterranean Chile. To this end, the hydrology of the Lonquén River is characterized, the relationship between streamflow and nutrients, solids, DOC, DOM properties is determined (through modelling, hysteresis and correlation) and the nutrient, solid and DOC loads are calculated for three rainfall events.

Materials and methods

Study area

The Lonquén River basin is located in the dryland of the Coastal Mountains in central Chile (36° 25' 59,88'' S; 72° 42' 0'' E). The river is predominantly intermittent, but there are some perennial streams in the basin (Duissaillant 2009). The basin has an irregular shape and drains an area of 1,075 km^2 (Fig 1). Its geomorphology is heavily weathered and of old relief, with granitic rocks and metamorphic slates. Its soils are eroded, with little permeability and high silt, clay and sand content (Duissaillant 2009). Land use in the catchment consists mainly mainly of forest plantations (*Pinus radiata* and *Eucalyptus globulus*) and agricultural monocultures, which are typical of the mediterranean climate of Chile (Hernández et al. 2016; Garfias et al. 2018). The annual average temperature is 14.1°C and annual rainfall is 897.9 mm (Duissaillant 2009).

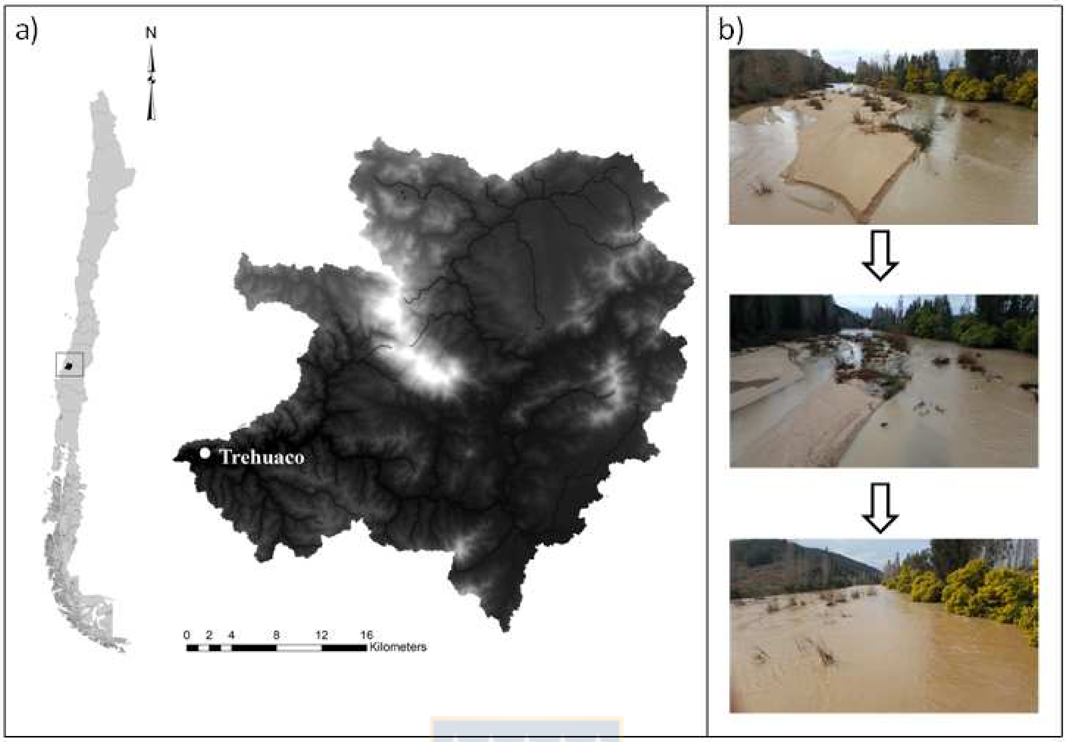

Fig. 1 a) Study area location b) Rain event stages in the Lonquén River basin, Trehuaco sector.

Hydrology

The study area rainfall and streamflow data was collected from the San Agustín de Puñual weather station and Lonquen station of the Chilean General Water Directorate (2019) (DGA, for its initials in Spanish).

The flow of the Lonquén River is intermittent; in winter there is heavy precipitation and in summer extreme droughts. The dry period begins in late December and lasts until approximately June, when the flow becomes fragmented, with the formation of isolated pools in some stretches.

Based on the information from the San Agustin de Puñual weather station (DGA), the antecedent precipitation index (API), which allows the rain-runoff relationship to be modeled and soil moisture prior to storms to be determined, was calculated (Bruce and Clark 1966; Perrone and Madramootoo 1998). This index was calculated for the three rainfall events included in our study, as follows:

$$API = k * P_1 + k^2 * P_2 + \ldots + k^n * P_n \qquad (1)$$

Where P_1, P_2,…, P_n are precipitation depths, 1, 2,…, n are the days prior to the event and k is a constant (k=0.85). There are three classifications of antecedent moisture, in accord with the API value: condition 1: 0 ≤ API ≤ 15 mm (dry); condition 2: 15 ≤ API ≤ 30 mm (average) and condition 3: API > 30 mm (wet).

Sampling and chemical analysis

The river water was sampled every two hours during three storm events in 2015 in a section located in the Trehuaco Commune (Fig 1): Storm 1 (August 6-7); Storm 2 (August 25-27); and Storm 3 (September 23-25), for a total of 17, 20 and 19 samples, respectively. In each sampling the variables pH, conductivity, dissolved oxygen and temperature were measured *in situ* using a multiparameter sonde (Hydrolab Quanta multiparameter). In addition, surface water samples were taken for analysis of DIN, TP, TN, SS, DS and DOC and optical analysis to characterize organic matter (Table 1).

The samples for nitrate (NO_2^-), nitrate (NO_3^-) and ammonium ions (NH_4^+) were filtered *in situ* (Durapore PVDF de 0.45 µm). Subsequently, the anions (NO_2^- and NO_3^-) and cations (NH_4^+) were analyzed in DIONEX ICS-2000 and DIONEX ICS-2100 chromatographs, respectively. DIN was calculated as the sum of N-NO_2^-, N-NO_3^- and N-NH_4^+ concentrations.

TP was preserved *in situ* with 2 mL 95-97% sulfuric acid, and TN and TP were analyzed in a Perkin–Elmer Lambda 25 UV–vis spectrophotometer. The water samples for SS were filtered using a glass fiber filter (0.45 µm GF/F). The filtered volume varied according to the quantity of SS, reaching a maximum of 2000 mL; the sediment retained in the filter was dried in an oven for 48 H at 60°C. The filtered liquid was dried for 48 h at 100°C to determine DS (APHA 2017).

The water samples for DOC and optical analysis were filtered *in situ* (pre-combusted Whatman GF/F 0.7 µm glass fiber filter), acidified (pH=2) and kept cold until their analysis in the Shimadzu TOC analyzer. To describe organic matter five optical indices were used, three chromophoric – (i) specific ultraviolet absorbance at 254 nm (SUVA), (ii) intensity ratio of absorbances (E_2:E_3) and (iii) spectral slope ratio (S_R), analyzed in a UV1700 Pharma Spec spectrophotometer (Shimadzu) – and two fluorophobic – (i) biological index (BIX) and (ii) microbial index (*β/α*), analyzed in an RF-5301 PC spectrofluorometer (Shimadzu). The absorbance and fluorescence indices used are described in Table 1.

Table 1 Description of the optical indices used to characterize the dissolved organic matter in this study.

Index	Calculation	Description	Reference
$SUVA_{254}$	UV absorbance at a wavelength of 254 nm normalized for dissolved organic carbon (DOC) concentration.	SUVA is a parameter for estimating the dissolved aromatic carbon content in aquatic systems.	Weishaar et al. 2003
E_2:E_3	The ratio of absorbance at 250 nm and 365 nm.	Index related to the average molecular size of DOM; the lower E_2:E_3, the higher the molecular size.	De Haan and De Boer 1987
S_R	Ratio of absorbance spectra slopes; 275–295 nm and 350–400 nm.	Slope ratio (Sr) is a proxy for the apparent DOM molecular weight; high values indicate DOM with low molecular weight.	Helms et al. 2008
BIX	The ratio of fluorescence intensity emitted at 380 nm divided by fluorescence intensity emitted at 430 nm at excitation 310 nm.	Index of recent autochthonous contribution (by autotrophic productivity); with high values of BIX meaning high autochthonous DOM.	Huguet et al. 2009
β/α	The ratio of fluorescence intensity emitted at 380 nm divided by the maximum emission intensity between 420 nm and 435 nm at excitation 310 nm.	The ratio of β/α is an indicator of autochthonous inputs and provides an indication of the relative contribution of recently microbially produced DOM. Fluorescence index and β/α values increase with in-creasing autochthonous carbon production.	Parlanti et al. 2000 Wilson and Xenopoulos 2009

The loads for the three events were calculated for DIN, TN, TP, DOC, SS, and DS using the Walling and Webb (1985) method:

$$Load = V * \frac{\sum_{i=1}^{n}(Ci * Qi)}{\sum_{i=1}^{n} Qi} \qquad (2)$$

Where Ci is the solute concentration of the point sample (mg L^{-1}), Qi is point streamflow in each sample (m^3 s^{-1}), V is the water volume in the entire study period (m^3) and n is the number of samples.

Data analysis

Significant differences in streamflow and variables among the three rainfall events were determined via a Shapiro and Wilk (1965) normality test and subsequent ANOVA or Kruskal-Wallis analysis as appropriate. These differences were represented by a star plot graphed using Infostat. The relationship between streamflow and all the studied variables was found by the coefficient of determination from polynomial fits and the *p* value associated with the adjusted model. The relationship among streamflow, nutrients and

DOC was analyzed through hysteresis, with the hysteresis pattern existing when the concentrations of a solute at a given streamflow are different in the rising and falling limbs of the hydrograph and allowing the solute source to be identified. A clockwise trend indicates solute dilution, but this dilution trend can also be observed in the flow versus concentration graph, when the concentration of a solute increases rapidly at the beginning of an event, and in the same way its concentration decreases during the rest of the episode.The relationship between DOC and the optical properties of DOM was obtained through Pearson correlation. All the analyses were carried out in R version 3.1.1, using the lm, vegan and performance analytics packages.

Results

Hydrology, streamflow and variable relationship

According to the historical streamflow station data, the baseflow of the river fluctuates between 0 and 10 $m^3 s^{-1}$, while the mean monthly streamflow is 13.07 $m^3 s^{-1}$. During 2015 the surface flow reconnection began on July 10 and lasted until December 11, when a new fragmentation cycle began. In that period minimum streamflows of 0.48 $m^3 s^{-1}$ and maximums of 273.1 $m^3 s^{-1}$ were presented. The three rainfall events, S1, S2 and S3, presented swells of various magnitudes, with maximum streamflows of 178.6, 170.3 and 45.5 $m^3 s^{-1}$, respectively (Fig 2). The antecedent moisture conditions (API) indicated that prior to the first event soil conditions were wet, unlike the dry conditions before events 2 and 3 (Table 2). However, there are greater significant differences when comparing all the variables and greater similarity between the first and third event ($p<0.05$). The first even had a more elevated streamflow and DIN and the second had higher TN, DS, SS, TP and DOC concentrations (Fig. 2, Table 2).

The highest solute loads were transported in the first two rainfall events. DIN, TN, DS and DOC transport was higher in the first rainfall event (Table 2). Meanwhile, the SS and TP loads were higher in the second event, with 2322 and 4 tons transported, respectively. According to the modeling, temperature was related to streamflow in the first event (Table 3). DIN, DOC and S_R were significantly related to streamflow in all three rainfall events, and this relationship was greater in the second and third events. TN, conductivity, pH, DO, TP, SS, DS, *β/α*, BIX, E_2:E_3 and $SUVA_{254}$ were related to streamflow in the last two events (Table 3).

Relationship amomg nutrients, DOC, optical properties of DOM and streamflow determined via hysteresis

In the first rainfall event all the variables (TN, TP, SS, DS and DOC) except DIN presented a clockwise pattern, with a consequent flushing of these solutes (Fig 3). In the second event all the variables had a clockwise trajectory (dilution). In the third event no hysteresis effect was observed because samples were taken only from the rising limb of the storm hydrograph.

The proxies (Table 1) and DOC followed a different pattern in the three storm events. During the rising limb of the hydrograph in the first rainfall event (Fig 4), the DOC concentration decreased and autochthonous DOM due to both microbial (*β/α*) and autotrophic activity (BIX) increased. The molecular weight of DOM also increased (S_R).

Meanwhile, a decrease in the molecular size (E_2:E_3) and aromaticity of DOM ($SUVA_{254}$) was observed. In the falling limb of the hydrograph in the first event, as well as the rising limb of the second event, there was an increase in the DOC concentration and the molecular size (E_2:E_3) and aromaticity of DOM ($SUVA_{254}$), with autochthonous DOM (β/α and BIX) and molecular weight of DOM (S_R) decreasing (Fig 4).

In the falling limb of the second event, the DOC concentrations and autochthonous DOM (β/α and BIX) decreased; smaller molecular size (E_2:E_3) and lower aromaticity ($SUVA_{254}$), but greater molecular weight of DOM (S_R), were observed.

During the rising limb of the third event, the DOC concentration increased and autochthonous DOM (β/α and BIX) decreased. Aromaticity ($SUVA_{254}$) and molecular size (E_2:E_3) increased and molecular weight (S_R) decreased until the streamflow reached 15 m^3 s^{-1}.

Table 2 Hydrological and biogeochemical variables during storms 1, 2 and 3 in the Lonquén River. Antecedent precipitation index (API), temperature (T), conductivity (Cond), dissolved oxygen (DO), dissolved inorganic nitrogen (DIN), total nitrogen (TN), dissolved solids (DS), suspended solids (SS), total phosphorus (TP) and dissolved organic carbon (DOC). Different letters indicate significant differences ($p<0.05$).

	Storm 1				Storm 2				Storm 3				*p* value between storms		
Date	6-7/08/2015				25-27/08/2015				23-25/09/2015						
API (mm)	32.40 (wet)				13.30 (dry)				9.00 (dry)						
Variable	Mean	D.E.	Load (tons)		Mean	D.E.	Load (tons)		Mean	D.E.	Load (tons)		S1 vs S2	S1 vs S3	S2 vs S3
Discharge ($m^3 s^{-1}$)	144.74	30.37	-	a	99.46	62.37	-	a	14.17	13.61	-	b	0.0842	<0.0001	0.0001
pH	6.48	0.11	-	c	8.38	0.14	-	a	7.11	0.03	-	b	<0.0001	<0.0001	<0.0001
T (°C)	12.43	0.77	-	b	11.89	0.61	-	b	13.80	1.33	-	a	0.0969	0.0001	<0.0001
Cond (µS cm^{-1})	0.10	0.01	-	a	0.07	0.01	-	b	0.11	0.02	-	a	0.0001	0.2355	<0.0001
DO (mg L^{-1})	13.52	1.36	-	a	12.29	1.55	-	a	10.37	0.25	-	b	0.1286	<0.0001	<0.0001
DIN (mg L^{-1})	0.52	0.04	9.6	a	0.20	0.03	1.4	b	0.11	0.03	0.3	c	<0.0001	<0.0001	<0.0001
TN (mg L^{-1})	0.98	0.34	18.3	a	1.23	0.46	9.4	a	0.48	0.23	1.2	b	0.2033	0.0002	<0.0001
TP (mg L^{-1})	0.09	0.07	1.8	b	0.51	0.32	4	a	0.25	0.14	0.6	b	<0.0001	0.0316	0.0003
SS (mg L^{-1})	36.77	33.16	93.00	b	343.26	326.70	2322.00	a	130.31	85.96	327.40	a	<0.0001	0.0016	0.1716
DS (mg L^{-1})	130.06	35.94	2434.50	b	174.65	34.60	1320.30	a	114.00	18.72	217.50	b	0.0001	0.1223	<0.0001
DOC (mg L^{-1})	2.75	0.61	49.50	b	4.08	0.64	32.40	a	2.85	0.96	6.4	b	<0.0001	0.7074	<0.0001
β/α	0.52	0.02	-	a	0.49	0.02	-	b	0.51	0.02	-	a	<0.0001	0.0645	0.0223
BIX	0.53	0.02	-	a	0.50	0.02	-	b	0.52	0.02	-	a	<0.0001	0.0624	0.0278
E_2:E_3	4.18	0.39	-	ab	3.96	0.56	-	b	4.59	0.79	-	a	0.0611	0.3902	0.0047
S_R	0.95	0.06	-	a	0.89	0.07	-	b	0.86	0.10	-	b	0.0143	0.0018	0.4469
$SUVA_{254}$	11.95	2.43	-	ab	13.48	3.49	-	a	10.55	2.93	-	b	0.1418	0.1897	0.0055

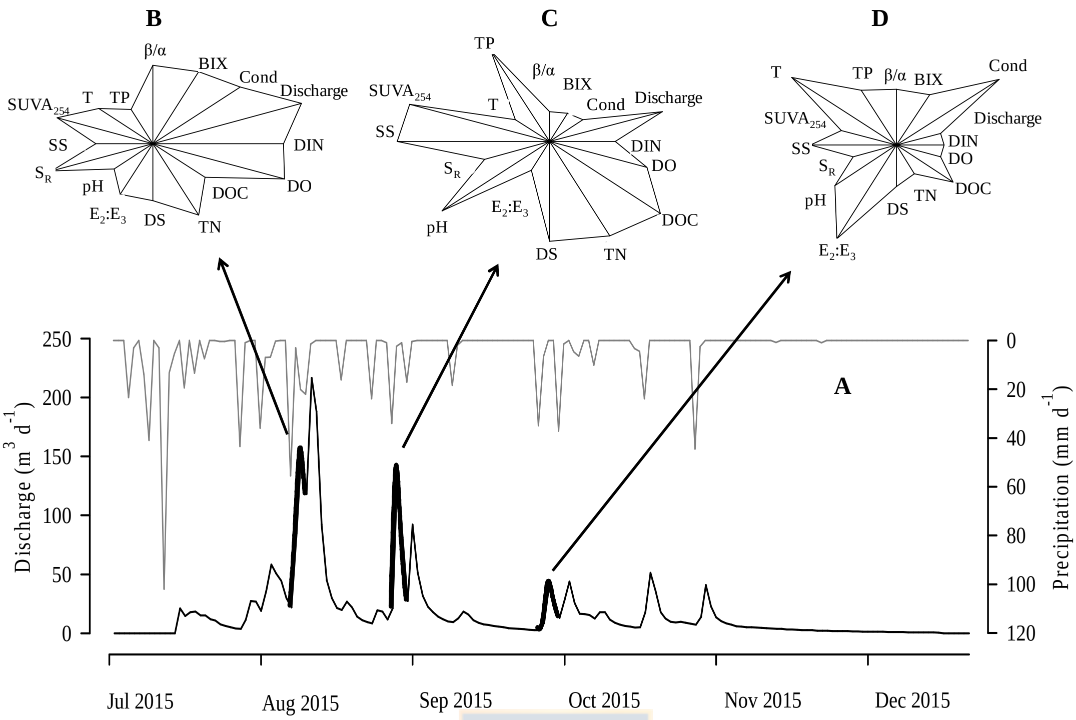

Fig. 2 (A) Daily precipitation (gray), mean daily flow (black) and three sampled storms (thick black lines). (B), (C) and (D) they are the star graphics for each rain event, where the length of each line with respect to the center represents the rescaled value of each variable.

Relationship between DOC and optical properties of DOM

There is a significant correlation in the study period between the proxies that characterize DOM (Table 1) and DOC concentration (Table 4). It was observed that an increase in DOC concentration is related to a decrease in autotrophic DOM resulting from microbial (*β/α*) and autotrophic activity (BIX) (p<0.05), and that the increase in the molecular size of DOM (E_2:E_3) is related to greater aromaticity ($SUVA_{254}$) and lower molecular weight of DOM (S_R) during the three rainfall events (Table 4).

Table 3. Polynomial adjustment model of the coefficient of determination (R^2), p values of the adjusted model (Model) and the estimated polynomial coefficients (D, D^2 and D^3) between streamflow and physical-chemical variables, nutrients, solids and optical properties of DOM derived from measurements of fluorescence and absorbance: pH, temperature (T), conductivity (Cond), dissolved oxygen (DO), dissolved inorganic nitrogen (DIN), total nitrogen (TN), total phosphorus (TP), suspended solids (SS), dissolved solids (DS), dissolved organic carbon (DOC), freshness index (β/α), index of recent autochthonous contribution (BIX), index of molecular size (E_2:E_3), slope ratio (S_R) and aromatic DOM ($SUVA_{254}$). Bold numbers indicate significant values (p<0.05).

	Storm 1				Storm 2					Storm 3				
	R^2	Model *p* value	D	D^2	R^2	Model *p* value	D	D^2	D^3	R^2	Model *p* value	D	D^2	D^3
pH	0.16	0.1156			0.75	**<0.0001**	0.1252	0.0245	0.0161	0.36	**0.0288**	0.0123	0.0090	
T	0.55	**0.0037**	0.0011	0.0014	0.02	0.5157				0.19	0.0646			
Cond	0.26	0.1171			0.90	**<0.0001**	<0.0001	0.0001	0.0004	0.96	**<0.0001**	<0.0001	0.0021	0.0077
DO	0.06	0.3358			0.80	**<0.0001**	0.0073	0.0091	0.0231	0.22	**0.0425**	0.0425		
DIN	0.25	**0.0415**	0.0415		0.62	**<0.0001**	<0.0001			0.79	**<0.0001**	<0.0001		
TN	0.01	0.7325			0.80	**<0.0001**	<0.0001	0.0001	0.0008	0.64	**0.0003**	0.0018	0.0134	
TP	0.07	0.3217			0.64	**0.0009**	0.0021	0.0135	0.0461	0.75	**0.0001**	0.0005	0.0078	0.0381
SS	0.03	0.5126			0.86	**<0.0001**	<0.0001	<0.0001	0.0001	0.78	**<0.0001**	<0.0001	<0.0001	
DS	0.01	0.6491			0.85	**<0.0001**	<0.0001	0.0005	0.0063	0.92	**<0.0001**	<0.0001	<0.0001	0.0005
DOC	0.48	**0.0138**	0.0082	0.0060	0.86	**<0.0001**	<0.0001			0.97	**<0.0001**	<0.0001	0.0024	0.0133
β/α	0.01	0.7245			0.49	**0.0009**	0.0009			0.76	**<0.0001**	0.0001	0.0006	
BIX	0.01	0.7172			0.55	**0.0003**	0.0003			0.73	**0.0001**	0.0002	0.0012	
E_2:E_3	0.02	0.5589			0.80	**<0.0001**	<0.0001	0.0003	0.0013	0.66	**0.0013**	0.0003	0.0010	0.0033
S_R	0.35	**0.0130**	0.0130		0.57	**0.0049**	0.0017	0.0041	0.0091	0.79	**0.0001**	0.0001	0.0002	0.0010
$SUVA_{254}$	0.00	0.8052			0.61	**0.0021**	0.0023	0.0121	0.0350	0.83	**<0.0001**	<0.0001	<0.0001	0.0002

Table 4 Matrix of correlation between DOC and optical properties of DOM during the three rainfall events: dissolved organic carbon (DOC), freshness index (β/α), index of recent autochthonous contribution (BIX), index of molecular size (E_2:E_3), DOM molecular weight (S_R) and aromatic DOM ($SUVA_{254}$) (bold values indicate a significant relationship, $p<0.05$).

	Storm 1					Storm 2					Storm 3				
	β/α	BIX	E_2:E_3	S_R	$SUVA_{254}$	β/α	BIX	E_2:E_3	S_R	$SUVA_{254}$	β/α	BIX	E_2:E_3	S_R	$SUVA_{254}$
DOC	**-0.74**	**-0.78**	**-0.54**	-0.18	**0.66**	**-0.63**	**-0.67**	**-0.60**	0.09	0.32	**-0.79**	**-0.78**	-0.29	-0.01	0.31
β/α		**0.98**	0.48	0.00	**-0.52**		**0.98**	-0.05	**0.60**	0.33		**0.99**	0.44	-0.19	-0.40
BIX			**0.51**	0.00	**-0.54**			-0.01	**0.54**	0.28			0.43	-0.19	-0.40
E_2:E_3				**-0.62**	**-0.88**				**-0.76**	**-0.84**				**-0.89**	**-0.93**
S_R					0.35					**0.79**					**0.91**

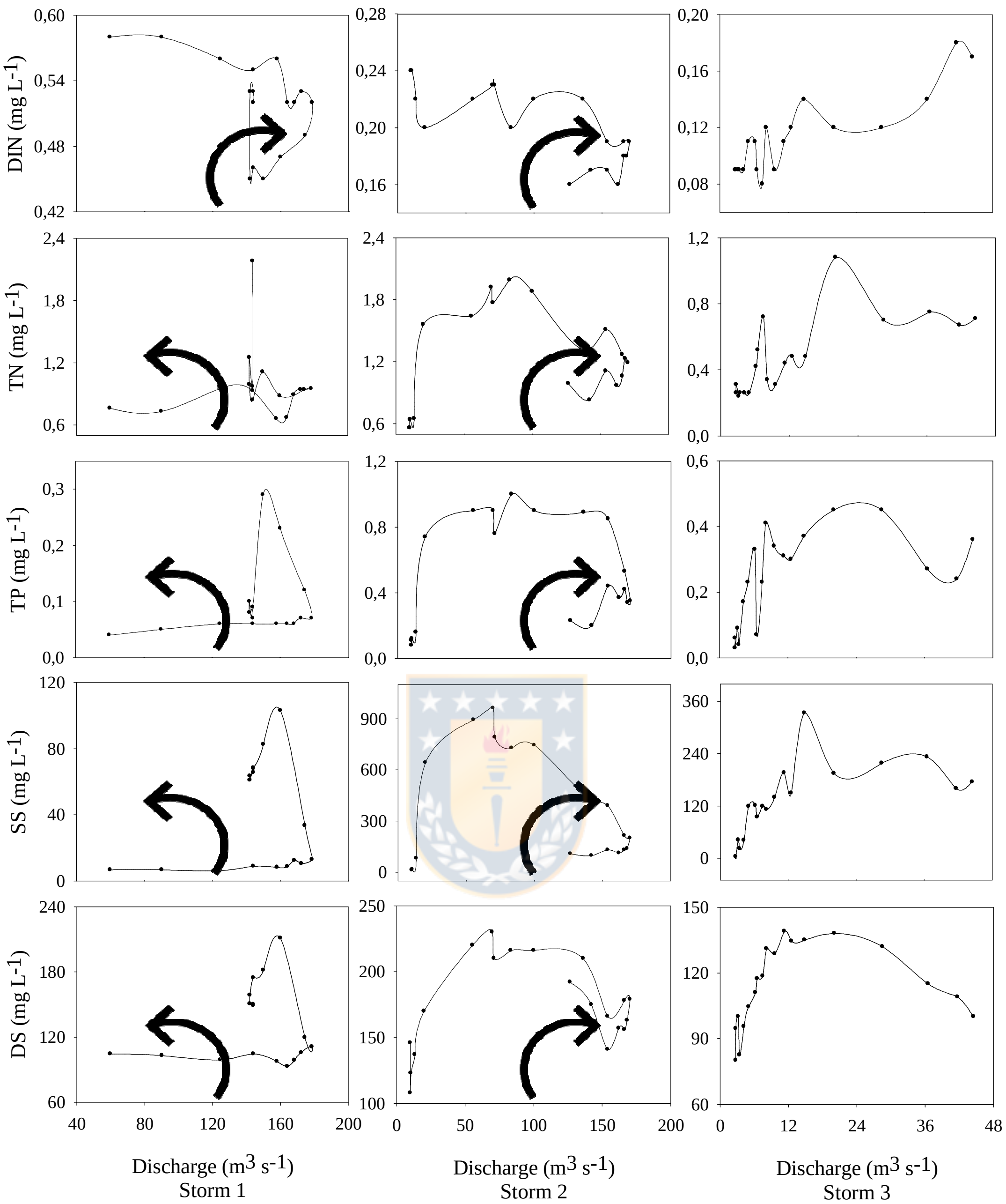

Fig. 3 Relationship between nutrients and solids and discharge: dissolved inorganic nitrogen (DIN), total nitrogen (TN), total phosphorus (TP), suspended solids (SS) and dissolved solids (DS).

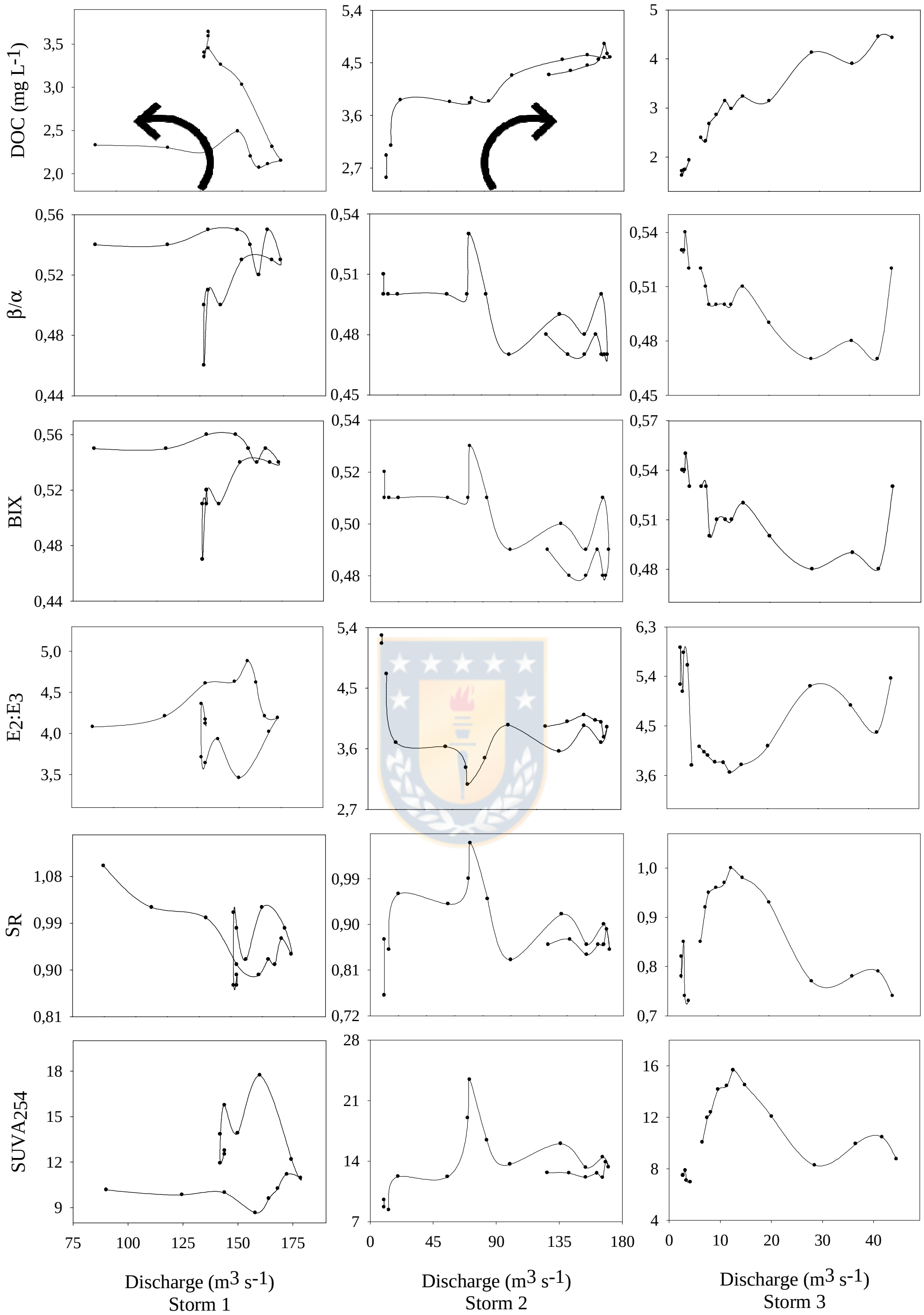

Fig. 4 Relationship between DOC and organic matter descriptor indices and discharge: dissolved organic carbon (DOC), freshness index (β/α), index of recent autochthonous contribution (BIX), molecular size index (E_2:E_3), slope ratio (S_R) and specific UV absorbance at 254 nm ($SUVA_{254}$).

Discussion

Relationship among hydrology, streamflow and variables

Many studies have related streamflow to nutrients (Chen et al. 2012; Du et al. 2014; Bowes et al. 2015; Edokpa et al. 2015; Lloyd et al. 2016), sediment load (Arias et al. 2013; Cerro et al. 2013; Ramos et al. 2015) and DOC (Buffam et al. 2001; Butturini et al. 2008; Fasching et al. 2016; Guarch-Ribot and Butturini 2016). According to our modeling results, the variables of conductivity, DIN, DOC and slope ratio (S_R) are strongly related to streamflow. In some cases, the relationships could not be explained by the model, as occurred in the first rainfall event with temperature, because its variation was related to the time of day at which the sample was taken, with the greatest value measured during the afternoon and the lowest observed at night.

Long-term studies (Cerro et al. 2013; Bowes et al. 2015; Lloyd et al. 2016) and other short-term evaluations (Du et al. 2014) have found a close relationship between streamflow and phosphorous, TN and solids, observing an increase in these variables at high streamflows and a rapid reduction at a reduced flow. In our study, this relationship was observed only in the second and third event. Likewise, it was observed that the DIN concentration generally decreases as streamflow increases, which does not coincide with other studies (Chen et al. 2012; Edokpa et al. 2015).

The DOC concentration was related to streamflow during the three events (Table 3), a tendency observed in other studies (Buffam et al. 2001; Butturini et al. 2008; Cerro et al. 2014; Edokpa et al. 2015; Fasching et al. 2016). However, in our study, DOC concentrations were lower than those found by Guarch-Ribot and Butturini (2016), but consistent with studies in which it was found that streamflow influences the type of carbon the basin is transporting. For example, the streamflow increase in some cases is related to the increase in the DOC concentration and weight and aromaticity of DOM (Fellman et al. 2009; Guarch-Ribot and Butturini 2016; Shumilova et al. 2019).

High streamflows can transport a large quantity of solutes (Rovira and Batalla 2006), impeding their processing but contributing nutrients and organic matter downstream (Buffam et al. 2001; Ensign and Doyle 2006). In general, rainfall events transport large quantities of sediment, carbon and nutrients. For example, Ramos et al (2015) determined that storm events can account for over 90% of TP transport during a hydrological year, while nitrate transport during rainfall events accounts for about 60% of the total annual load. Our results indicate high variability in the transport of solutes between and during rainfall events, as also found by Oeurng et al (2011), as well as elevated dissolved solid and suspended solid transport during the three events. This phenomenon was also reported by Ramos et al (2015), showing that storm events can account for 85% of solute transport during a hydrological year. However, lower carbon, solid and nitrogen loads were transported during each event in our study area compared to transport in a perennial river in an agricultural basin. The studied storm events transported lower quantities of solutes than what was reported by Oeurng et al (2010, 2011), possibly because although the Lonquén River basin is used for agriculture, few fertilizers are added and it presents significant erosion and low soil organic matter content. However, a high capacity for transporting solutes during rainfall events stands out; they are an essential source of energy for heterotrophic bacteria in the river and coastal (Scherer et al. 1984; Austin et al. 2004; Sponseller 2007; Paerl 2009; McLaughlin and Kaplan 2013; Raymond et al. 2016).

Relationship between streamflow and nutrients, DOC and optical properties of DOM determined via hysteresis

The hysteresis pattern exists when solute concentrations at a given streamflow are different in the rising and falling limbs of the hydrograph, an effect that has been well described in previous studies and is essential for identifying solute sources (House and Warwick 1998; Bowes et al. 2005; Chen et al. 2012; Du et al. 2014). In the first two events the DIN supply originated in mobilization within the river channel and was diluted by the increase in streamflow, reaching its peak during the rising limb of the storm hydrograph. This pattern was also found by Bowes et al. (2015) for nitrate, indicating groundwater as the main source of this nutrient. Ramos et al. (2015) also observed this effect, but in the first storm events recorded in autumn, where in general there was flushing behavior, as was observed by Pellerin et al. (2012). In the first rainfall event, all the variables except for DIN presented a counterclockwise trajectory, indicating that the peak concentrations occurred during the falling limb of the hydrograph, flushing the solutes through surface runoff and delivering them in a delayed manner downstream. Our TP and SS results are comparable to those of Ramos et al. (2015), who described a predominant flushing of these particulate solutes. Moisture conditions prior to the first event could explain the flushing of the studied solutes. In addition, precipitation prior to the event and the consequent increase in soil humidity could have influenced the transport of dissolved solids and DIN from the flushing of the riverbed.

In the second event, all the variables had a clockwise trajectory, characterized by the dilution of solutes that possibly come from the same river channel and groundwater. Similar results were obtained by Bowes et al. (2015) for total reactive phosphorous (TRP); here phosphorous was removed mainly from the riverbed (bed sediments) at elevated streamflows. In addition, each storm tends to present unique hysteresis characteristics that can be associated with various parts of the year, solute type (dissolved or suspended), soil moisture or storm degree (Bowes et al. 2015; Chen et al. 2012; Du et al. 2014).

Relationship between DOC and optical properties of DOM

During the rain events, the sources and characteristics of carbon can change rapidly and are a transitory but important pathway in carbon transport (Pellerin et al. 2012; Jung et al. 2012; Raymond et al. 2016). According to our study, there was a high correlation between DOC and the proxies that characterize DOM, as well as DOC and streamflow. In general, an increase in streamflow means that the quantity of nutrients and allochthonous organic matter increases (Bernal et al. 2013), as occurred in the second event. However, a prior long-term study in Mediterranean Europe did not identify a predictable pattern in the relationship between DOC and streamflow (Butturini et al. 2008). Other studies have found coupling of the proxies that characterize DOM and streamflow (Fellman et al. 2009; Pellerin et al. 2012; Fashing et al. 2016).

Therefore, analyzing the behavior of DOM properties in relation to streamflow is a challenge, as in this study it is more related to DOC concentrations in water than to streamflow dynamics. This analysis becomes more complex under a climate change scenario, which is affecting the hydrology of mediterranean rivers, especially in Chile, one of the 10 most affected countries, which has undergone a reduction in precipitation and an increase in temperatures (IPCC 2014; Delgado et al. 2015; Welz 2016), phenomena that can affect DOC and nutrient concentrations and DOM properties.

Conclusions

The three studied storm events transported large quantities of solutes, as well as suspended and dissolved solids. In addition, the modeling analysis reflects a close relationship in the three events between streamflow and most of the variables, especially DOC, making it potentially useful in future studies.

Hysteresis is a good method for determining solute dilution or flushing in rainfall events, the only limitation of which is methodological, as it requires continuous sampling of the variables throughout the storm hydrograph. Moisture conditions prior to the event and the magnitude of precipitation during the storm can be determinant in the behavior of the variables. The rainfall event with the most intense precipitation generated flushing of almost all the solutes, while in the second case, less intense precipitation during the storm diluted them, possibly because it provided aquifer recharge, whose subsequent input to the river generated solute dilution. The studied correlations between DOC and properties of DOM indicate that there are relationships between these variables; therefore, DOC can be a predictor of organic matter properties in rainfall events.

The Lonquén River responds to the various characteristics of the basin, such as its land use and soil type, addition of fertilizers and intensity and quantity of precipitation before and after the rainfall event. Therefore, it is not possible to generalize patterns for each variable, which demonstrates the need for continuous, longer-term studies that would allow a greater capacity for management, especially amid the uncertainty of climate change that will affect the mediterranean climate to a greater extent than others.

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DISCUSIÓN GENERAL

Los ríos intermitentes son sistemas fluviales altamente dinámicos que sostienen fases hidrológicas marcadas por el cese del flujo de aguas durante algunos días o meses (Larned et al., 2010; von Schiller et al., 2011; Benstead y Leigh 2012). Son ecosistemas que drenan una gran proporción de los biomas terrestres en todos los continentes y tipos de clima (Stanley et al., 1997; Larned et al., 2010; Acuña et al., 2014; Datry et al., 2014). Además, los ríos intermitentes están aumentando en longitud y extensión global debido al cambio climático y presión antropogénica (Jaeger et al., 2014; Datry et al., 2016).

En el río Lonquén, los episodios de sequía comienzan a inicios del verano, con el incremento de la temperatura atmosférica, que bordea una máxima de 40°C y la reducción de las precipitaciones. El caudal se reduce considerablemente, y el lecho del río comienza a secarse, pero en ocasiones se mantienen pozas de gran tamaño entre los tramos secos, así como algunos arroyos perennes que tributan al río principal. Debido el escaso o nulo caudal, se acumula materia orgánica en el lecho del río, que proviene principalmente de la vegetación de ribera, así como de árboles y arbustos que crecen dentro del cauce (Brintrup et al., 2019).

La acumulación de material vegetal terrestre depende del aporte de la vegetación ribereña, mediada por su retención, duración de la fase seca, topografía del canal y la composición de la vegetación ribereña que depende de los regímenes de flujo, el que a su vez varía según el clima (Datry et al., 2018). En este sentido, el clima Mediterráneo de Chile propicia la acumulación de hojarasca de buena calidad, debido a la condición ecológica de los ecosistemas fluviales y al alto nivel de endemismo de la vegetación ribereña (Palma et al., 2009; Figueroa et al., 2013; Boyero et al., 2017). Una vez que se acumula en el cauce, la materia vegetal es sometida a fotodegradación y/o biodegradación, según sean las condiciones de humedad y luz del lecho del río (Austin y Vivanco 2006; Corti y Datry 2012; Brintrup et al., 2019).

La cuenca del río Lonquén, incluye arroyos intermitentes y perennes de cobertura ribereña típica mediterránea (Palma et al., 2009; Figueroa et al., 2013; Boyero et al., 2017), propiciando lechos sombríos y en ocasiones húmedos, además, la duración prolongada del periodo de sequía favorece la acumulación de materia orgánica de alto potencial productivo, en comparación con los perennes (Hoover et al., 2006; Richardson et al., 2009; Brintrup et al., 2019).

La materia vegetal que se acumula en los lechos de ríos perennes tiene el potencial de emitir grandes cantidades de CO_2 atmosférico (Raymond et al., 2013; Hotchkiss et al., 2015), ya que la humedad y nutrientes estimula la descomposición por microbios y detritívoros invertebrados (Gessner et al., 2010; Boyero et al., 2011; Raymond et al., 2013). Los productos que se liberan luego de este proceso son fuente de energía y base para las cadenas tróficas, procesos ecosistémicos y el ciclo del carbono (Gessner et al., 2010; Boyero et al., 2011). Para el caso de los ríos intermitentes, tanto el procesamiento del material vegetal y la emisión de CO_2 atmosférico que se genera a partir de él, han sido escasamente estudiados y por lo mismo, desestimados del balance global del carbono (Battin et al., 2009; Raymond et al., 2013; Butman et al., 2016).

Tras la rehumectación del primer pulso de inundación, se activa el procesamiento bacteriano rápidamente, por lo cual IRES son catalogados como reactores biogeoquímicos (Datry et al., 2016), es así como los ríos intermitentes en solo un pulso de inundación pueden generar el equivalente al 10% de las emisiones diarias de CO_2 que los ríos perennes emiten en un año (Datry et al., 2018). Por lo tanto, es error desestimar a los ríos y arroyos intermitentes del balance global de C, más aún cuando los estudios actuales han considerado las emisiones que se generan en un pulso de inundación y estos resultados podrían ser más importantes, dado que el paso siguiente es cuantificar la emisión de CO_2 durante la reanudación del flujo *in situ* (Corti y Datry 2012), en fase seca (Gómez-Gener et al., 2016) y en presencia de flujo continuo (Raymond et al., 2013).

Este antecedente es relevante en Chile Mediterráneo, especialmente donde existe cobertura ribereña, que sumado a extensos periodos de fase fragmentada, propician una elevada acumulación de materia vegetal de alto potencial productivo (Brintrup et al., 2019) y posiblemente de buena calidad, es decir con baja proporción de N:P (Palma et al., 2009; Figueroa et al., 2013; Boyero et al., 2017; Datry et al., 2018). Pese a lo esperado, los ríos intermitentes estudiados en Chile registran emisiones en promedio de 539.37 mg. CO_2 m^{-2} d^{-1}, valor que se encuentra bajo la media mundial que corresponde a 883.19 mg. CO_2 m^{-2} d^{-1} (Datry et al., 2018), aunque hay ríos de Chile, que emiten 2555.4 mg. CO_2 m^{-2} d^{-1}, valor que se encuentra sobre la media mundial. Por lo cual se requieren más estudios que aborden toda la gama del mediterraneo chileno.

Durante la fase de fragmentación del río Lonquén se mantienen condiciones muy particulares y distintas a las descritas en otros IRES (Vidal-Abarca et al., 2000; Acuña et al., 2005; Lillebo et al., 2007; von Schiller et al., 2011; Katipoglu et al., 2012), donde el nivel de oxígeno en las pozas es muy bajo, favoreciendo procesos anaeróbicos como la amonificación y desnitrificación (Lillebo et al., 2007; Puckett et al., 2008; Krause et al., 2009; von Schiller et al., 2011; Katipoglu et al., 2012), propiciando la liberación de fósforo desde el sedimento del lecho del río hacia el agua superficial de las pozas. En cambio, en el área de estudio, éstas conservan una profundidad y productividad primaria que permite una temperatura y nivel de oxígeno óptimo para la conservación de alguna flora y fauna, como macroinvertebrados bentónicos, peces y macrófitas, con una zona hiporreica activa.

A principios de otoño, la temperatura atmosférica disminuye y las precipitaciones son más frecuentes, incrementándose el nivel freático, así como el tamaño de las pozas, propiciando una mayor interacción entre el agua superficial y subterránea, e incrementando el nivel de oxígeno en la zona de hiporreo (Corti y Datry 2012; Arce et al., 2014). Posteriormente, los eventos de lluvia más intensos reconectan el río en un primer pulso de inundación en la fase de rehumectación, y el material vegetal acumulado durante los meses secos es transportado aguas abajo, además de nutrientes, carbono y sólidos (Corti y Datry 2012). En este primer pulso, generalmente la concentración de nutrientes es elevada, ya que el nitrógeno y fósforo que se acumuló en el agua intersticial del sedimento y en las pozas es resuspendido y liberado a la columna de agua y agua subterránea (Butturini et al., 2003; Arce et al., 2014).

Sin embargo en el río Lonquén las concentraciones de nutrientes, como DIN no difieren significativamente entre las pozas y flujo de reconexión, por lo que es posible que esta carga es abatida rápidamente en el pulso de inundación por bacterias de la zona del hiporreo, ya que esta zona es el compartimento biogeoquímico más dinámico del río (Dahm et al., 2003; Daesslé et al., 2017), donde existen microorganismos altamente adaptados al estrés hídrico y a las características del sedimento (Fierer y Schimel 2002; Fierer et al., 2003). Esto también permite plantear que la escasa variabilidad entre el agua superficial y de hiporreo se deba a la continua relación entre ellas incluso en fase de fragmentación. En la reconexión del agua superficial, el peak de la concentración de P es más bajo que N, esto se explica por la alta cantidad de N liberado desde el sedimento y suelos en condiciones aeróbicas, además de la dilución de P por el incremento del caudal y su rápido consumo (Baldwin et al., 2000; Tzoraki et al., 2007; von Schiller et al., 2011). Destaca también una elevada concentración de SS en el primer pulso de inundación, fenómeno frecuente en otras cuencas erosionadas (Obermann et al. 2009; Skoulikidis y Amaxidis 2009).

Posteriormente, y de acuerdo a la particularidad del año hidrológico, ocurren eventos de precipitación de diversa frecuencia y magnitud en otoño e invierno. Independiente de cómo ocurra este proceso, los eventos de tormenta transportan gran cantidad de solutos (nutrientes, SS, materia y carbono orgánico) (Bowes et al., 2009, 2011; Oeurng et al., 2011; Gao et al., 2012; Roach 2013; Raymond et al., 2016; Lloyd et al., 2016). Pero una disminución de DIN, patrón también encontrado en otros estudios (Buffam et al., 2001; Butturini et al., 2008; Chen et al., 2012; Cerro et al., 2013; Du et al., 2014; Bowes et al., 2015; Edokpa et al., 2015; Fasching et al., 2016; Lloyd et al., 2016). La remoción de solutos que provienen desde la cuenca, son arrastrados por escorrentía hacia el río, y también pueden ser aportados por el lecho del río y agua subterránea (Bowes et al., 2015; Ramos et al., 2015), a excepción de DIN que proviene siempre desde el lecho y agua subterránea. Por lo tanto, cada tormenta tiene características únicas de histéresis que pueden estar asociadas a la época del año, el tipo de soluto (disuelto o suspendido), humedad del suelo o grado de la tormenta (Chen et al., 2012; Du et al., 2014; Bowes et al., 2015).

Para determinar el origen de los solutos es importante obtener registros durante todo el hidrograma de tormenta, para un correcto análisis de la relación caudal-concentración. Durante el incremento del caudal en los eventos de lluvia, la calidad de la materia orgánica disuelta es predominantemente aromática, más liviana, de mayor tamaño, y menos autóctona (Fellman et al., 2009; Guarch-Ribot y Butturini 2016; Shumilova et al., 2019). Así como la fuente de los solutos varía en cada evento, las características de la materia orgánica pueden cambiar rápidamente (Pellerin et al., 2012; Jung et al., 2012; Raymond et al., 2016), y se ha demostrado que está altamente correlacionado a la concentración de DOC (Fellman et al., 2009; Pellerin et al., 2012; Fashing et al., 2016), como ocurre en el río Lonquén.

Para cada análisis en las distintas fases del río Lonquén y otros intermitentes, es necesario analizar las características meteorológicas de la cuenca (Bruce and Clark 1966; Perrone and Madramootoo 1998), ya que pueden proporcionar datos sobre un posible comportamiento durante la fase de fragmentación, vale decir mayor o menor humedad en tramos secos impacta sobre la descomposición o fotodegradación de la materia orgánica, así como en la emisión de CO_2 en la fase de rehumectación y reconexión del sistema, como también puede influir en la cantidad y origen de materia orgánica, nutrientes y solutos que se transportan en esta fase. En eventos de lluvia, el análisis de las precipitaciones previas y durante el evento, nos pueden proporcionar información sobre el origen y cantidad de los solutos transportados y características de la materia orgánica.

A fines de la primavera, el sistema retoma su caudal base, donde el continuo fluvial es muy similar a un río perenne (Vannote et al., 1980), posteriormente vuelve a fragmentarse, generando reactores biogeoquímicos puntuales, propiciando la acumulación de materia vegetal en el lecho del río (Larned et al., 2010; Datry et al., 2018; Brintrup et al., 2019). Mientras los ríos perennes procesan durante todo el año la materia orgánica que ingresa al continuo fluvial, en IRES la materia organica se acumula durante varios meses, hasta que en la fase de rehumectación, junto al primer pulso de inundación es procesada rápidamente y se liberan al continuo fluvial gran cantidad de nutrientes, carbono, energía y emisiones de CO_2 a la atmósfera (Larned et al., 2010; Datry et al., 2018).

En este sentido, diversas presiones como el cambio climático, cambios de uso de suelo y las presiones de uso del agua, que afectarán en mayor medida a regiones con alta demanda hídrica asociado a la productividad agrícola y el crecimiento demográfico, podría implicar un incremento en la cantidad, longitud de los ríos intermitentes, de igual modo se incrementará el periodo de sequía en IRES. Además, muchos ríos perennes serán intermitentes en el corto y mediano plazo (Larned et al., 2010; Stehr et al., 2010; Acuña et al., 2014; Creed et al., 2017). Esta situación es particularmente grave en Chile, porque es uno de los países más vulnerables al cambio climático (Vicuña et al., 2012; IPCC 2014), además no hay una reglamentación que proteja a IRES y lamentablemente, los derechos de agua que ya son cuestionados por científicos y la ciudadanía como base de la gestión, no es adecuada para estos sistemas y por lo tanto, es necesario abordar el funcionamiento biogeoquímico de IRES de manera más profunda, siendo este una primera aproximación para Chile, que permitirá comprender el funcionamiento de otros IRES e ir generando una línea base para su protección.

CONCLUSIÓN

1. La primera hipótesis se cumple, ya que los ríos intermitentes estudiados acumulan gran cantidad de materia orgánica de alto potencial productivo. La segunda hipótesis se cumple parcialmente, porque en la rehumectación IRES de Chile emiten CO_2 atmosférico, pero con una tasa inferior al promedio global, además, el primer pulso de inundación no siempre implicó un incremento en la concentración de las variables, se observa un alza importante en sólidos y fósforo, pero disminución de TN en el agua superficial, y en hiporreo no hay diferencias. La tercera hipótesis se cumple, dado que durante eventos de lluvia el caudal sí puede ser usado como predictor de las variables.
2. Los IRES no están siendo considerados en el balance global del ciclo del carbono, lo que podría ser un grave error, por las altas tasas de CO_2 atmosférico que emiten, aunque en Chile la media sea inferior al promedio global.
3. Las pozas que permanecen durante la fase de fragmentación en el río Lonquen, mantienen condiciones disimiles de otros IRES del mediterráneo Europeo, ya que en general son de gran tamaño, con niveles elevados de oxígeno y, una zona hiporreica activa, ligada a reacciones bacterianas aeróbicas. Sin embargo, las pozas podrían reducir sus niveles de oxígeno debido al cambio climático y favorecer procesos como la desnitrificación y liberación de P por desorpción.
4. Durante el primer pulso de inundación, la materia orgánica acumulada es transportada aguas abajo, pero la respuesta biogeoquímica difiere mucho en cada tramo, pese a eso generalmente hay nutrientes que se mantienen estables en las pozas y durante la reconexión (DIN), esto es atribuible a la capacidad de resiliencia de las bacterias del hiporreo que transforman rápidamente los nutrientes liberados al agua superficial durante el primer pulso de reconexión.
5. En los eventos de tormenta que proceden la reconexión del sistema, el caudal puede ser un importante predictor del origen, concentración de solutos, y propiedades de la materia orgánica. Histéresis es un buen método para determinar la dilución o arrastre de un soluto en eventos de lluvia, su única limitación es metodológica, ya que requiere de muestreos continuos a través de todo el hidrograma de tormenta.
6. Los IRES ocupan parte substancial de las cuencas en todo el mundo, y se estima que tanto su extensión como el periodo de intermitencia aumente debido al calentamiento global y presiones antropogénicas. Este fenómeno afectará a Chile en mayor medida, ya que es uno de los países más vulnerables al cambio climático. Sin embargo, aun no hemos cuantificado este impacto en términos de valores actuales y proyecciones futuras, asi como en el funcionamiento biogeoquímico e implicancia de cada una de las fases en IRES. Dado que este es el primer trabajo en esta línea, se manifiesta la necesidad de efectuar estudios espaciales y temporales continuos, para generar base de datos que faciliten la gestión y así formular políticas de protección para el agua superficial y del lecho del río, hoy altamente explotado para usos agrícola del sector.

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