



Nitrogen processing following experimental sediment rewetting in isolated pools in an agricultural stream of a semiarid region



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ABSTRACT

Water scarcity represents an important driver of stream microorganisms and N transformations rates. In semiarid regions many agricultural streams rich in NO_3^- undergo periods of flow cessation of severe duration and spatial extent. After drought, rainfalls tend to firstly rewet stream sediments by creating isolated pools that can remain in streambeds until the entire stream is reconnected. Sediment rewetting may lead the reactivation of nutrient processing, yet usually causes release of inorganic N. Thus, information about the role of sediments during this rewetting period on N processing and fluxes downstream is especially valuable when semiarid watercourses are affected by chronic NO_3^- exposure.

We conducted a microcosm study to evaluate how a short-term sediment rewetting over a 7 days period in disconnected pools can control denitrification rates and N availability in an agriculturally impacted semiarid stream.

We observed a significant stimulation of denitrification in dry sediments ($<0.01 \mu\text{g N m}^{-2} \text{h}^{-1}$) upon rewetting with a maximum rate of $830 \mu\text{g N m}^{-2} \text{h}^{-1}$ after 24 h. In parallel, NO_3^- in dry sediments (1170 mg m^{-2}) dropped considerably after 7 days of rewetting (72 mg m^{-2}), despite the fact that denitrification was restrained from 24 h thereafter. However, from this time a notably increase of NH_4^+ concentration was detected until the end, which suggests that at this point, NO_3^- is transformed into NH_4^+ through dissimilatory reduction (DNRA) supported by low Eh (40 mV). If compared with NO_3^- , NH_4^+ can be either more easily retained in sediments or assimilated preferably by organisms. We highlight that the diversification of N species provided by isolated pools creation just before flow resumption may progressively improve water quality in NO_3^- -rich streams, which is a key aspect in the face of future agriculture intensification and water scarcity scenario.

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1. Introduction

In the last few decades, increasing agriculture intensity and extension have dramatically increased nitrogen (N) loading to aquatic ecosystems (Bernot and Dodds, 2005). In terms of landscape-level N cycling, streams are considered important sites as they can transform and retain N through different in-stream processes (Alexander et al., 2009), reducing the export of excess N to downstream ecosystems (Hall et al., 2009). The massive change in N cycling has stimulated the interest of researchers and managers in understanding how streams can regulate the dominant inorganic form, nitrate (NO_3^-). From a stream water

quality perspective, denitrification is comparably the most desirable pathway since this mechanism represents the only permanent N sink through the conversion of NO_3^- into gaseous N forms under low oxygen conditions (i.e., N_2O and N_2). The contribution of denitrification to mitigate excess NO_3^- is especially relevant in agricultural landscapes where streams undergo high NO_3^- inputs (Lassaletta et al., 2009).

Given their natural low discharge and relatively scarce stream biomass, streams of arid and semiarid climates have been recognised as being especially vulnerable to NO_3^- saturation (Arce et al., 2013). Particularly in the Southern Iberian Peninsula, water NO_3^- concentrations in downstream reaches can become chronically high (up to 20 mg L^{-1}) as a result of steady agricultural pressure (Arce et al., 2013). As with most Mediterranean streams, streams draining this semiarid region are temporary as they periodically cease to flow (Gasith and Resh, 1999). Temporary streams currently account for likely more than 50% in the global fluvial network and are expanding in response to global change

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(Larned et al., 2010; Datry et al., 2014). However, information about functional aspects, such as in-stream N processing and its link with hydrology, is still limited (von Schiller et al., 2011; Gómez et al., 2012; Arce et al., 2014a). As described in aridland soils (Schwinning and Sala, 2004; Collins et al., 2008), N transformation rates in temporary streams may be spatially and temporarily discontinuous due to stream water is highly heterogeneous in both space and time (Stanley et al., 1997; von Schiller et al., 2011). Compared with wet phases, streambeds are seen as biogeochemically quiescent during dry periods as water scarcity represents a significant physiological stress for soil biota and slows down microbial activity (Fierer et al., 2003; Amalfitano et al., 2008). Nonetheless, despite diminished microbial activity, increasing oxic conditions in desiccated sediments may favour aerobic pathways such as nitrification; the oxidation of ammonium (NH_4^+) to NO_3^- , whereas denitrification is substantially reduced (Gómez et al., 2012) and restricted to suboxic and anoxic microsites where this process generally occurs (Seitzinger et al., 2006). Thus, continuous nitrification during a period of general low biological N demand can provide NO_3^- accumulates in stream sediments in extended dry phases (Gómez et al., 2012; Steward et al., 2012; Arce et al., 2014a). The drying pattern of most of temporary streams is structured longitudinally (Stanley et al., 1997) and dry event duration and frequency tend to increase with distance downstream along the temporary stream, presenting perennial, intermittent and ephemeral sections (Larned et al., 2010). In Mediterranean semiarid streams, surface flow is especially heterogeneous in space and time, thus intermittent sections, which undergo recurrent wet and dry phases, are common along the entire stream channel and dry phases are not only restricted to summer. Rainfall events taking place over a year rarely re-establish stream flow in intermittent sections. Instead, these rainfalls usually generate water runoff that reaches streambeds and frequently results in the creation of disconnected pools scattered throughout the desiccated streambed. Such pools may represent biogeochemically important sites or "hot spots" (McClain et al., 2003) in semiarid streams and have important implications for stream water quality and nutrient transport downstream. The latter could be especially true during the first steps of stream flow resumption when pools are connected and the surface flow along the section is continuous, which predominantly occurs in spring and late autumn in Mediterranean areas (Machado et al., 2011). Sediment rewetting may result in a release of carbon (C) and inorganic N to stream water column (Baldwin et al., 2005; Butterly et al., 2009) that may potentially move downstream if flow resumes. Indeed, last studies conducted in Mediterranean temporary catchments have reported initial flood events (following dry periods) with high water nutrient concentrations (Obermann et al., 2009; Skoulikidis and Amaxidis, 2009). Natural peaks in water nutrient concentrations in temporary streams might modify momentarily the ecological status in the context of the European Water Frame Directive by changing the physico-chemical water quality (Sánchez-Montoya et al., 2012). The release of NO_3^- accumulated in desiccated sediments upon rewetting could be involved in such natural peaks (Gómez et al., 2012; Arce et al., 2014a) and have significant consequences for surface water quality in agricultural watersheds where high NO_3^- levels of runoff water may lead NO_3^- transformation rates to approach saturation. Rewetting of dry sediments has been shown to rapidly stimulate denitrification in Mediterranean temporary streams (Arce et al., 2014a) however, its implication to modulate the potential NO_3^- release is poorly understood. Thus, the punctuated activation of denitrification during sporadic rewetting in agricultural sites of semiarid zones could be a key aspect to alleviate potential export of NO_3^- downstream ecosystems when isolated pools are further reconnected and flowing water is re-established.

In this study, we conducted a microcosm experiment to simulate dry streambed rewetting in isolated pools using sediments from an agriculturally affected and intermittent reach. Our aims were to evaluate (i) changes in N availability in sediment and the water column following rewetting and (ii) the response and time over which sediment denitrification responds to this water pulse. Since N dynamics is strongly linked to organic C availability (e.g., Arango et al., 2007), we also explored how organic C availability varied following sediment rewetting.

Based on previous evidence (Gómez et al., 2012; Arce et al., 2014a), we expected a substantial NO_3^- release from sediments to the water column after the rewetting of dry sediments in the microcosms. We also predicted that sediment denitrification would rapidly be activated after water arrival, thus modulating NO_3^- availability in the microcosms water column.

2. Material and methods

2.1. Site description

The sediments used in this study were collected from an intermittent reach of the Chicamo stream ($38^\circ 12'44'' \text{N}$, $1^\circ 03'07'' \text{W}$, 173 m asl) (Fig. 1), a temporary stream which drains a watershed of 501.8 km². The study site is characterised by a semiarid Mediterranean climate and presents average annual temperature and precipitation of $\sim 18^\circ \text{C}$ and of <300 mm, respectively, and an annual evapotranspiration >900 mm. The selected reach presents an intermittent flow, and despite being variable over years, dry periods usually begin from late June to early July, and continue until late October or November when the stream flow is usually restored. During dry periods, sporadic rainfall results in water runoff that rewet sediments creating isolated pools that are scattered along streambeds (Fig. 1), and that can remain wet before they are reconnected when flow resumes following heavy rains. Riparian vegetation is very scarce and dominated by Mediterranean shrubs, including *Tamarix canariensis* and sporadic halophytic plants such as *Suaeda vera* and *Limonium* sp. The land use of the draining watershed is a mixture of agriculture (43%; irrigated farms and ponds) and forest (52%; grasslands and Mediterranean shrubs), where most irrigated farms are condensed in the down part of the watershed (Arce et al., 2013). As a result of the irrigated agriculture and low discharge (2.3 L s^{-1}) in the study reach, the average water dissolved organic C (DOC) and nutrient concentrations are high under baseline flow conditions ($\text{DOC} = 1.6 \text{ mg L}^{-1}$; $\text{NO}_3^- = 4.2 \text{ mg L}^{-1}$; $\text{NH}_4^+ = 0.02 \text{ mg L}^{-1}$) (Gómez et al., 2012). Chicamo is a saline stream (water conductivity up to 30 mS cm^{-1}) due to the presence in the catchment of sedimentary marls that are rich in NaCl and CaSO_4 . The main ion contributing to salinity is Cl^- following of Na^+ and SO_4^{2-} (557, 473 and 310 mg L^{-1} of average, respectively) (Arce et al., 2013). Presence of submerged macrophytes and allochthonous organic matter is generally null, and the biofilm covering the streambed accounts for most primary production and constitute the main source of labile C (Vidal-Abarca et al., 2004; Gutiérrez-Cánovas et al., 2009).

2.2. Microcosms set-up

To run the microcosm experiment, wet sediments were collected from the study site under pre-dry conditions when the surface water flow started to cease (July 2009). Sediments were collected along a 50-m length from the top 5 cm. Sediments were well mixed and placed randomly in 21 microcosms (transparent plexyglass tanks $28 \text{ cm} \times 18 \text{ cm} \times 15.5 \text{ cm}$ deep), which were transported to the University of Murcia outdoor premises. Microcosms were kept air-dried for a desiccation period lasting up to 3 months, which is the usual dry period length of the Chicamo

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