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Development of Innovative Nutrient Removal Substrates for Mediterranean River Restoration

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Abstract

Aquatic ecosystems eutrophication is a worldwide pollution problem in which nitrification plays a major role. Riparian buffer zones along river corridors may help to mitigate the effects of non-point source pollution. However, riparian zone variability affects the rate of nitrate removal because the major pathway for nitrate movement is through subsurface flow. Therefore, in areas where the water table is relatively close to the surface, denitrification may be enhanced by increasing the contact between shallow groundwater and carbon-rich areas that can support denitrification. One way to achieve that is through bioreactors, in which a substrate is in contact with the agricultural effluent. This study addresses the use of innovative materials as substrates for denitrification walls in a Mediterranean context. Therefore, different materials will be tested using a column adsorption apparatus. The experiment will be repeated over a range of nitrate concentrations for each substrate, using different effluent flowrates. A lysimeter field trial will be performed using the most suitable substrate from the column test. In addition, the efficacy of denitrification walls as a management tool will be evaluated through the application of the MOHID process-based model to a watershed, the Sorraia basin.

Keywords: bioreactor; denitrification; eutrophication; filters; nitrates; river restoration; substrates.

Introduction, scope and main objectives

Many aquatic ecosystems suffer from eutrophication (Jørgensen et al. 2013). High concentrations of nitrate in the water have negative effects in health and are associated with diseases such as stomach cancer and cardiac disease (Townsend et al. 2003). Therefore, a limit for nitrate concentration in potable water of 50 mg NO_3^-/L was adopted in the European Union (Drinking Water Directive 98/83/EC). The development of cheap water treatment chemicals has been of great interest during the past decade (Keränen et al. 2013). Bio-based materials offer a local, renewable and low-cost raw material for the production of water treatment chemicals (Keränen et al. 2013). Wood based solid carbon substrates that simultaneously serve as a biofilm carrier and as a source of organic carbon for denitrification are being used in bioreactors worldwide (Greenan et al. 2009, Schipper and Vojvodić-Vuković 1998). Cheap woody substrates, with high long term nitrate removal rates, are required in order to have efficient bioreactors and to keep costs as low as possible. Therefore, there is a need to test new and more cost efficient bio-materials, like cork and amended woody materials. This work addresses that need by studying the nitrate removal capability of several innovative denitrification substrates in a Mediterranean river basin context.

With this work we aim to: i) study the nitrate removal capability of several innovative denitrification substrates in laboratory, using small bioreactors to simulate a denitrification wall; ii) test the field-scale nitrate removal efficiency of the best suited substrate on a lysimeter station, under Mediterranean conditions; iii) predict groundwater NO_3^--N flow through the riparian zone and denitrification wall for the Sorraia river valley using a software model.

Methodology/approach

In order to achieve the proposed objectives, the experimental work will be divided into three main tasks.

- **Task 1: Column adsorption tests with different inert woody materials.**

Laboratory column tests will be undertaken to assess nitrate removal potential of several candidate organic carbon substrates for use in denitrification filters. The experiment will take place in a continuous column apparatus, fed through a peristaltic pump in the bottom, discharging at the top via a drainage line, with sampling ports at 20 cm intervals along its length (Robertson 2010) (Figure 1). The tested substrates will be cork, pine sawdust and two different amended substrates: chemically modified pine sawdust (Keränen et al. 2013, 2015) and a combination of woodchip and maize cob (Warneke et al. 2011). Each substrate will be mixed in a 1:2 ratio with material from the C and A soil layers and loaded into the column. The media will be compacted at 3-5 cm increments to ensure a tight matrix and will fill the column into its top (Robertson 2010). The control media will be composed only by soil from the C and A horizons. Distilled water amended with NO_3^--N (KNO_3) will be pumped through the columns. The flowrate through the column will be set to simulate typical groundwater velocity conditions in the Sorraia river valey (Gavaskar 1999), using soil saturated conductivity data adapted from (Cameira et al. 2003). Tests will take place using different influent NO_3^- concentrations and flowrates. Samples will be analyzed for NO_3^--N and NH_4^{+4}-N concentrations, dissolved organic carbon (DOC) and dissolved oxygen (DO).

- **Task 2: Lysimeter adsorption tests.**

The leaching rate and migration time of NO_3^--N through a denitrification filter using Sorraia river valley soil profiles will be tested in a lysimeter test station (22 PVC lysimeters). The Sorraia basin was selected because it suffers from strong agricultural related anthropogenic perturbations. Because NO_3^- removal rates tend to decline with time as labile C is reduced (Schipper and Vojvodić-Vuković 1998), the experiment will take place for at least 12 months, in order to reliably assess the long term sustainability of NO_3^- removal rates (Schipper et al. 2010). The denitrification filter will be prepared using material from the A and C soil layers mixed in a 2:1 proportion with the substrate selected after the conclusion of Task 1. The control treatment (without filter) will consist on a layer of sieved homogenized mineral soil of the C horizon placed over the drainage system of each lysimeter. A layer of the A soil horizon will be placed on top of the C layer material. Both layers will be packed at a bulk density similar to the one measured at the site of origin of the material. Tests will take place using different nutrient loads (KNO_3) and irrigation levels. Bromide will be added to the nutrient load (1:1 mixture of KNO_3:KBR) as a conservative, noninteractive tracer to determine which physical processes contribute to reduction in NO_3^- concentrations (Nelson et al. 1995). The rate of movement of Br^- in soil mimics that of NO_3^--N and it is a biologically and chemically stable ion (Kessavalou et al. 1996). Thus, changes in the NO_3^--N/Br^- ratio indicate whether nitrate depletion is the result of dilution or evapotranspiration rather than microbial transformations or gaseous losses (Nelson et al. 1995). Samples will be analyzed for NO_3^--N and NH_4^{+4}-N concentrations.

- **Task 3: Application of a simulation model that estimates the denitrification wall removal capability under different nutrient loads for the Sorraia river valley.**

In order to simulate groundwater NO_3^--N flow through the riparian zone and denitrification wall, we will apply a process-based software model to the Sorraia river valley. The efficacy of denitrification walls will be evaluated through the simulation of different irrigation levels and nutrient loads. The model input data will be divided into three main classes: flow properties (water content of the soil, water fluxes and the pressure and hydraulic conductivity in each grid point), properties transportation by the flow (simulates the advection/diffusion of solutes), and transformation of the transported properties (including the root activity and adsorption/desorption). Soil fertilization and irrigation will be approached as system boundaries.

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