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Evaluation of two carbon sources for inducing denitrification: Batch and column experiments.

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Abstract

Artificial recharge improves several water quality parameters. Denitrification is a good example of water treatment process that could be achieved through artificial recharge. To improve the removal of nitrate and other emerging organic contaminants (EOCs) a reactive barrier at the bottom of an infiltration pond can be added. In the present study, the efficiency in removing nitrate of an artificial recharge system with a compost layer located in the Mediterranean area (Sant Vicenç dels Horts, Catalonia) is evaluated, as well as the feasibility of another carbon source to be used as reactive layer in the artificial recharge system planned in the Maghreb Region. We examined the effectiveness of two different materials, commercial compost and crushed palm tree leaves, in batch and column experiments. The results of batch experiments confirmed that both materials induced denitrification and the flow-through experiments showed complete nitrate removal. The isotopic fractionation of nitrogen and oxygen of dissolved nitrate was calculated for both experiments in order to provide a tool to evaluate the efficacy of the treatments in future field scale studies.

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1. Introduction

Managed aquifer recharge (MAR) is a worldwide used technique that consists on the purposeful recharge of an aquifer under controlled conditions to store water for later abstractions and/or to improve its quality[1,2]. MAR techniques are diverse: infiltration ponds, deep recharge wells and trenches among others. One of the most common methods for artificial aquifer recharge are infiltration ponds. These systems often have a decantation pond to improve water quality through the deposition of the suspended solids and avoid clogging. Additionally in infiltration ponds a reactive layer can be installed to create favourable conditions to induce biodegradation of a target contaminant/s.

The MAR system located in the Llobregat Delta (Catalonia, NE Spain) is an artificial recharge system that consists on a decantation pond and an infiltration pond, and is recharged with water from de Llobregat River. At the bottom of the infiltration pond, a vegetable compost layer was installed in order to create favourable conditions for contaminant biodegradation. This reactive layer consists on a mixture of commercial compost, aquifer material, clay and iron oxide to enhance natural attenuation of emerging organic contaminants (EOCs)[3,4]. Previous studies performed in this site[4] have showed that nitrate reducing conditions favoured selected EOCs degradation.

The study area in the Maghreb Region is characterized by scarce precipitation, low water infiltration into aquifers and high water demand for domestic and agricultural uses; furthermore, one of the main pollutants in the area is dissolved nitrate. In this area an artificial recharge system consisting of a decantation pond and an infiltration pond is planned. However, in the Maghreb area the proposed material for the reactive layer consists on autochthonous vegetal remains: crushed palm tree leaves.

In order to identify the denitrification processes stable isotopes of dissolved nitrate are used. Those are a useful tool since an increase in $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ of residual nitrate with decreasing nitrate concentrations is characteristic of kinetic isotope fractionation induced by the breakage of N-O bonds during denitrification[5]. The objectives of the present study are (1) to assess denitrification capacity of the commercial compost used in the Llobregat MAR system, (2) to determine the feasibility of a new material (palm tree leaves) to enhance nitrate removal and (3) to calculate N and O isotope enrichments factors associated with nitrate attenuation.

2. Experimental set-up

2.1. Batch experiments

Groundwater used in the experiments was from the Llobregat aquifer, mainly coming from river infiltration. Commercial compost was obtained from a composting plant located in Moià (Catalonia, NE Spain) and palm tree leaves were from Maghreb region. Triplicate batch experiments were performed in sterilized 500 ml glass bottles for each material studied (P- palm tree leaves and CC- commercial compost) (Table 1). In addition a 'sterilized control' (SC) was carried out adding autoclaved material (palm tree leaves) to autoclaved groundwater, and an 'absence control' (AC) was carried out only with groundwater. In all the experiments, 0.80 mM of NO_3^- was added. All batch experiments were set up in an anaerobic glove box with an Ar atmosphere to avoid the presence of O_2. Bottles were manually shaken once a day and aqueous samples (5 ml) were collected daily using sterile syringes. Samples were collected for anions and isotopic analysis ($\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate). The commercial compost experiments lasted 11 days whereas the palm tree experiments lasted 1 day.

2.2. Column experiment

Two flow-through experiments were carried out using glass cylindrical columns (30 cm high, 9 cm inner diameter), one filled with commercial compost and the other filled with crushed palm tree leaves. In both cases, the studied material was mixed with clean silica sand (Panreac®) to increase permeability. The experiments were set up and carried out in an anaerobic chamber with an Ar atmosphere to avoid the presence of O_2. The input water used in the experiments was collected from the Llobregat aquifer. The flow rate in the column experiments was controlled by a peristaltic pump (peristaltic Micropump Reglo Digital 4 channels ISMATEC). Eh, pH and conductivity were measured daily at the outflow water. Samples were collected for hydrochemical analysis (major and minor cations, anions, dissolved inorganic carbon (DIC), non-purgeable organic carbon (NPOC)) and isotopic analyses ($\delta^{15}N$ and $\delta^{18}O$ of dissolved nitrate, $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulphate, $\delta^{13}C$ of dissolved inorganic carbon).

Table 1. Experimental conditions of the batch experiments.

Code	Experiment	Contents of the incubation
CC-Commercial compost	Triplicate (1,2,3)	20 g commercial compost, 400 mL groundwater, 0.80 mM NO_3
SC-Palm tree	Sterilized control	11 g autoclaved crushed palm leaves, 400 mL sterilized groundwater, 0.80 mM NO_3
P-Palm tree	Triplicate (1,2,3)	11 g palm leaves, 400 mL groundwater, 0.80 mM NO_3
AC-GW	Absence control	400 mL groundwater, 0.80 mM-NO_3

3. Results

3.1. Batch experiments

The results of batch experiments confirmed that both materials induced denitrification. Figure 1 shows complete nitrate consumption in less than 12 days for commercial compost. An initial NO_3^- release by the compost of up to 2.58 mM was observed. Complete nitrate reduction was achieved in less than 20 hours for palm tree leaves with no significant initial NO_3^- release. In the sterilized control and absence control (AC) experiments, nitrate reduction did not occur.

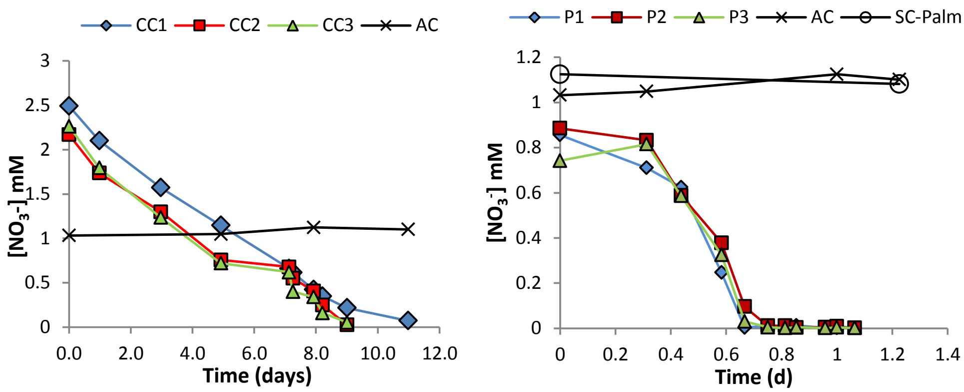

Fig. 1 Variation of nitrate concentration over time in batch experiments. Left: commercial compost triplicates (CC) and absence control (AC) experiments. Right: crushed palm tree leaves triplicates (P), absence control (AC) and sterilized control (SC) experiments.

The isotopic enrichment factors for N (εN) and O (εO) in the two amended batch experiments were calculated from the slope of the regression lines that fit the data of the natural logarithm of nitrate concentration vs. $\delta^{15}N$ or $\delta^{18}O$-NO_3^-, respectively. The values of εN (-15,49‰), εO (-9,05‰) and the εN/εO (1,71‰) ratio for the compost experiment confirmed denitrification. The isotopic results of the palm tree experiment were not conclusive since the rate of nitrate consumption was too fast, and nitrite accumulation was observed, causing analytical problems in the determination of $\delta^{18}O$-NO_3^-.

3.2. Column Experiments

Preliminary results of the flow-through experiments showed complete nitrate removal (Figure 2). In the commercial compost experiment complete nitrate removal was achieved after 10 days using groundwater with 0.81 mM NO_3^- as inflow water. An initial increase in nitrate concentration up to 4.84 mM was observed due to leaching as observed also in the batch experiment. In the palm tree experiment complete nitrate removal was achieved after 4 days using groundwater with 1.61 mM NO_3^- as inflow water. Nitrite accumulation up to 1.32 mM was also detected in commercial compost experiment and 0.06 Mm in palm tree experiment.

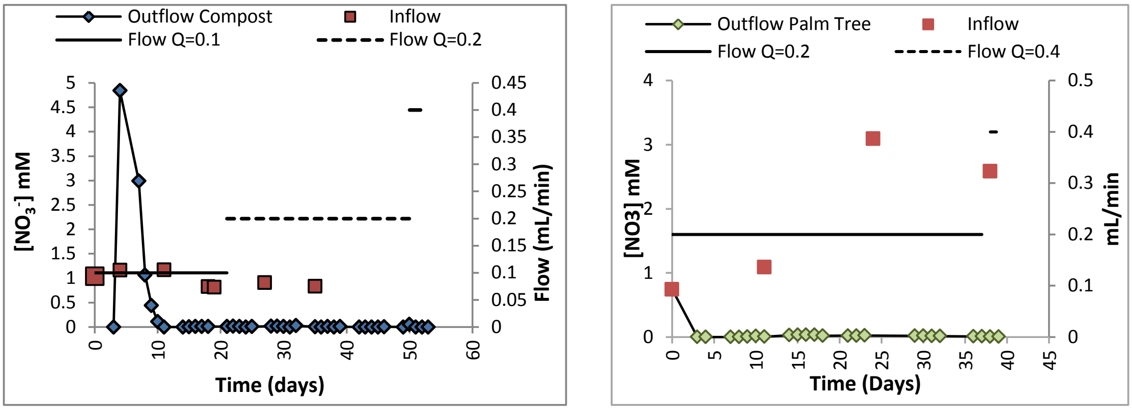

Figure 2. Nitrate concentration in the inflow (squares) and outflow water (diamonds) of the compost column and palm tree experiments. The flow rate is indicated with the horizontal lines

4. Conclusions

Batch and flow-through column experiments are a useful method to address the role of the different electron donors that can promote denitrification, to quantify the attenuation rates and to obtain isotope enrichment factors. The present work has evaluated two different carbon sources for inducing denitrification during MAR activities by means of batch and flow-through experiments. The experiments demonstrate that (1) the commercial compost enhanced nitrate reduction in both experiments (batch and column) although an initial release of nitrate was observed; (2) palm tree leaves were a good carbon source to induce denitrification although further studies should be performed in order to minimize nitrite production.

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