NITROGEN AND OXYGEN ISOTOPES OF DISSOLVED NITRATE TO EVALUATE THE EFFICIENCY OF INDUCED GROUNDWATER DENITRIFICATION AT FIELD-SCALE

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Nitrate (NO_3^-), one of the most common groundwater pollutants, can cause health problems in humans and contributes to the eutrophication of surface water bodies. Frequent sources of NO_3^- pollution are linked to extensive application of synthetic and organic fertilizers, inappropriate placement of animal waste and spills from septic system effluents. Throughout the last three decades anthropogenic nitrate inputs into our environment have significantly increased, giving rise to important loads of nitrate in surface water and groundwater in many parts of the world. Nitrate pollution has become a major threat to groundwater quality as the maximum nitrate concentration allowed by the European Directive 98/83/CE in waters for human consumption (50 mg/L) is reached in most of the regional aquifers in Europe.

Denitrification reaction is one of the most effective processes to remove NO_3^- pollution from groundwater. However electron donor availability (organic C or reduced S compounds) is usually a limiting factor in natural environments to achieve relevant natural NO_3^- attenuation (Knowles et al., 1982). To overcome this restriction, biostimulation of heterotrophic denitrifying bacteria by means of adding an external organic electron donor has been commonly used. Frequently tested electron donors include pure compounds such as alcohols (ethanol, methanol) or sugars (glucose, sucrose) or alternative sources of organic carbon such as compost or sawdust (Akunna et al., 1993; Trois et al., 2010; Grau-Martinez et al., 2017). Strategies aiming to fill the lack of electron donors have gained attention. Laboratory (Carrey et al., 2014; Torrentó et al., 2011) and small scale pilot sites (Vidal-Gavilán et al., 2013) have already demonstrated that adding an electron donor is adequate to induce nitrate attenuation in groundwater.

Nitrogen and oxygen isotopes of dissolved nitrate have been used to evaluate nitrate sources and natural attenuation processes (denitrification) in groundwater in several nitrate vulnerable zones (Otero et al., 2009, Torrentó et al., 2011, Puig et al., 2016). The isotopic fractionation of ^{15}N and ^{18}O that is produced during denitrification provides a tool to also estimate the efficacy of induced attenuation. The present study aims to evaluate the usefulness of stable isotopes of ^{15}N and ^{18}O of dissolved NO_3^- to trace denitrification efficiency in the course of a large-scale induced groundwater bioremediation project.

This study presents a denitrification pilot plant consisting of 2 injection, 3 monitoring and 1 extraction wells. Acetic acid was selected to stimulate and sustain intrinsic heterotrophic

denitrifying bacterial activity. A total of 42 samples were collected in 10 field campaigns from June 2015 to October 2016, and analysed for chemical and isotopic parameters. In addition, batch microcosm experiments using acetic acid as electron donor were performed. The batch experiments simulated aquifer conditions, using sediment and groundwater from the pilot plant test site. The aim of the batch experiments was to determine the isotopic fractionation of ^{15}N and ^{18}O.

The ε values determined in the batch experiments were -12.6‰ for N and -13.3‰ for O. The obtained isotopic fractionation values were applied to evaluate NO_3^- attenuation capacity of the pilot plant at field scale. The isotopic results of the pilot-plant showed that induced denitrification was produced, reaching a nitrate removal percentage of up to 50%. The highest attenuation was measured in the monitoring wells closer to the injection wells. In addition, the isotopic composition of ^{15}N and ^{18}O of nitrate suggested the occurrence of nitrite reoxidation. Nitrite is an intermediate compound of denitrification considered more toxic than nitrate. Hence, the observed reoxidation is a favorable process to avoid nitrite accumulation during induced attenuation treatment.

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References

Akunna, J.C., Bizeau, C., Moletta, R. (1993) Nitrate and nitrite reductions with anaerobic sludge using various carbon sources: glucose, acetic acid, lactic acid and methanol. Water research, 27: 1303-1312.

Carrey R., Otero N., Vidal-Gavilan G., Ayora C., Soler A., Gomez-Alday JJ (2104) Induced nitrate attenuation by glucose in groundwater: Flow-through experiment. Chemical Geology, 370: 19-28

Grau-Martínez, A., Torrentó, C., Carrey, R., Rodríguez-Escales, P., Domènech, C., Ghiglieri, G., Soler, A., Otero, N. (2017).- Feasibility of two low-cost organic substrates for inducing denitrification in artificial recharge ponds: Batch and flow-through experiments. J. Contam. Hydrology, 198, 48–58.

Knowles, R. (1982) Denitrification. Microbiological Reviews, 42: 43-70.

Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: the case of Plana de Vic (Osona, Spain).Agriculture Ecosystems Environment, V133, 103-113. (2009).

Puig, R.; Soler, A.; Widory, D., Mas-Pla, J.; Domènech, C.; Otero, N. (2016) Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer system (NE Spain) using a multi-isotope approach. Science of the Total Environment 580, 518 – 537.

Torrentó, C.; Urmeneta, J.; Otero, N.; Soler, A.; Viñas, M., Cama, J. Enhanced denitrification in groundwater and sediments from a nitrate-contaminated aquifer after addition of pyrite. Chem. Geol., 287, 90-101. (2011)

Trois, C., Pisano, G., Oxarango, L. (2010) Alternative solutions for the bio-denitrification of landfill lechates using pine bark and compost. J. Hazardous Materials, 178(1-3):1100-1105.

Vidal-Gavilán, G., Folch, A., Otero, N., Solanas, A.M., Soler, A., (2013) Isotope characterization of an in situ biodenitrification pilot-test in a fracture aquifer. Applied Geochemistry, 32: 153-163.