



## Hydrochemical and stable isotopic evaluation of denitrification in surface water in an agricultural catchment, Alentejo region, Portugal.

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This study explores the use of  $^{15}\text{N}$  and  $^{18}\text{O}$  isotopes of dissolved nitrate, ion tracers ( $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) and oxygen analysis in surface water from a stream network of an agricultural catchment (352 km $^2$ ), located in the semi arid Alentejo region in Portugal. From this agricultural catchment, water accumulates into a dam that provides water supply for drinking water to Beja City and irrigation, making it an important evaluation site for nutrients pollution. Therefore, the objective of this study is to identify the main nitrate sources and to asses the potential occurrence and degree of denitrification in surface water in two different seasonal periods, early autumn in October 2008 and early spring season in March 2009. Our results showed similar nitrate concentrations in both periods; however the highest concentrations registered in 2008 were recorded in the upper part of the stream network. Whereas the highest  $\text{NO}_3^-$  levels during spring 2009 were observed in the downstream area. The  $^{15}\text{N}$  and  $^{18}\text{O}$  isotope values of nitrate for surface water ranged from 3.02 - 15.3‰ and 4.29 - 30.9‰, respectively. In general, in the smallest streams nitrate has undergone significant denitrification, ranging from about 0 to 45% of the total samples. This is attributed to the presence of stagnated waters in some parts of the upstream and downstream sections, which act as nitrogen sinks. In October during dry autumn, the presence of high  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , low oxygen and low  $\text{NO}_3^-/\text{Cl}^-$  ratios registered can suggest some nitrate inputs from manure and sewage. During spring, when lower isotopic values of nitrate were presented high  $\text{NO}_3^-$  values were observed. One important portion of the isotopic data showed values related to fertilizer inputs, mainly during spring period, which is linked to fertilization applied during late winter (February-March), when precipitation is higher than the rest of the year. Whereas is known that microbial activity decrease in winter, thus these conditions would lead to less denitrification and increased leaching of  $\text{NO}_3^-$  from the soil during winter precipitation. The isotopic record suggested that part of the nitrate in the stream network is mainly derived from fertilizers and soil organic N, which agrees with some previous Nitrogen balance studies in the area. This research suggests that seasonal differences in the denitrification process should be considered into account when estimating local N budget.