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# Temporal analysis of spring water data to assess nitrate inputs to groundwater in an agricultural area (Osona, NE Spain)

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## HIGHLIGHTS

• Four different hydrological response types synthesise spring dynamics.
• Nitrate content remains steady despite rainfall events and fertilisation regimes.
• Temporal fluctuations in nitrate in aquifers could be attributed to groundwater withdrawal.
• Natural springs are indicative of the rate at which nitrate infiltrates into aquifers.

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## ABSTRACT

Non-point agricultural pollution is a major concern in groundwater management. To investigate nitrate input to the subsurface through groundwater recharge, thirteen natural springs were sampled. Discharge, electrical conductivity (EC), nitrate concentration, pH value and water temperature were monitored every two weeks from January 2010 till February 2011 at selected springs in the Osona region (NE Spain). Two extensive hydrochemical analyses were also conducted at the beginning and at the end of the survey. Springs are classified in four groups describing their hydrological response, based on discharge, EC and nitrate data. Geostatistical analysis provides an additional insight into the discharge and nitrate temporal pattern.
Even though discharge and EC can be related to specific hydrogeological behaviours, nitrate content shows uniform values in most of the springs with only a minor influence from external factors such as rainfall events, fertilisation regimes and geological traits. Such evenness of outflow might be attributed to a homogenisation of the subsurface processes that determine nitrate infiltration after decades of intensive fertilisation using pig manure. Accumulated nitrate mass load and variograms confirm this result. Assuming that spring data are representative of nitrate leaching towards the underlying aquifer, nitrate content of infiltrating recharge in shallow aquifers should therefore show a steady value over time with only small fluctuations due to natural processes. Nevertheless, temporal fluctuations in nitrate content in aquifers could be also attributed to flow regime alterations due to human groundwater withdrawal.


## 1. Introduction

Water pollution from non-point sources is a major concern in water management in most agricultural areas. Farming activities and other land uses have degraded the quality of aquifers by introducing large quantities of nutrients (Burg and Heaton, 1998; Buzek et al., 1998; Dietrich and Hebert, 1997; Focazio et al., 1998). In particular, Groundwater Directive 2006/118/EC (EC, 2006) considered nitrate to be one of the main contaminants that could impede the achievement of the objectives of Water Framework Directive 2000/60/EC (EC, 2000). It is also known that high levels of nitrate in groundwater are a human health concern (EEA, 2003). Some authors even claim that nitrogen compounds can act as human cancer promoters (Volkmer et al., 2005; Ward et al., 2005). For this reason, the World Health Organization (WHO, 2008) has promulgated a guideline of a maximum of 50 mg/L of nitrate in drinking water.

Springs provide sources of potable water and are of recreational, ecological and cultural value, but they also offer a way to assess groundwater quality because their discharge integrates, both spatially and temporally, groundwater from large parts of an aquifer (Katz et al., 2001). Springs represent the transition from groundwater to surface water (Kresic and Stevanovic, 2010) and are a direct reflection of the state of groundwater in the aquifers that feed them. The monitoring of springs can thus reveal the vulnerability of an

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area to a potential alteration to its groundwater resources (Elhatip et al., 2003; Katz et al., 2009; Leibundgut, 1998; Manga, 2001). Different studies, including Burg and Heaton (1998), Happell et al. (2006), Katz (2004), Katz et al. (1999, 2001, 2004) and Panno et al. (2001), have characterised nitrate occurrence and dynamics in springs using nitrate ions or isotopes as indicators of nitrate pollution. However, most of these studies describe large discharge springs, many of them located in karst systems, and little research has been done with regard to small discharge springs in semi-arid environments, associated with superficial, unconsolidated rock formations. For this reason, the hydrologic and hydrochemical behaviours of such springs has been characterised in 13 springs in the Osona region (NE Spain; Fig. 1) to explore their potential as a reliable measure of subsurface nitrate natural variability. Livestock and agricultural activities are very intensive in this region and it is therefore vulnerable to nitrate pollution from agricultural sources (European Nitrate Directive, 91/676/EEC; EC, 1991).

Menció et al. (2011a), Otero et al. (2009), Torrentó et al. (2011) and Vitòria et al. (2008) studied the nitrate occurrence in groundwater, its distribution, dynamics and natural attenuation from local and regional hydrogeological perspectives. Menció et al. (2011b) performed a logistic regression and ANOVA analysis to identify the importance of land use and geological setting in nitrate pollution in springs. According to them, high nitrate concentrations in Osona are commonly found in groundwater with average values in springs ranging from 8 to 380 mg $NO_3^-$/L, and in wells from 10 to 529 mg $NO_3^-$/L. Vitòria (2004) used $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ to confirm the link between groundwater nitrate pollution and pig manure. Manure is spread on the crops as organic fertiliser. The most common crop is wheat, grown on 30% of the total cultivated land (7219 ha), followed by barley (20%), corn (14%) and sorghum (5%), among other minor crops. Agricultural practices need to be considered because they may potentially influence nitrate concentration in groundwater. In the case of spring wheat and barley, application of slurry as a fertiliser takes place between mid-January and March, and for winter wheat and barley, from September to mid-December. Manure is applied to these crops between September and December. In the case of summer crops such as sorghum and corn, slurry fertilisation is from mid-January to July and manure application from January to mid-June.

The determination of the spatial distribution and temporal variability of hydrochemical constituents (whether natural or anthropogenic) in groundwater is recognised as a particularly useful correlative and interpretative tool that can provide valuable insight into the natural physicochemical processes which govern groundwater chemistry (Davison and Vonhof, 1978). Time series analyses can be used to demonstrate the trend and temporal structure of a data set (Hipel and McLeod, 1994; Worral and Burt,

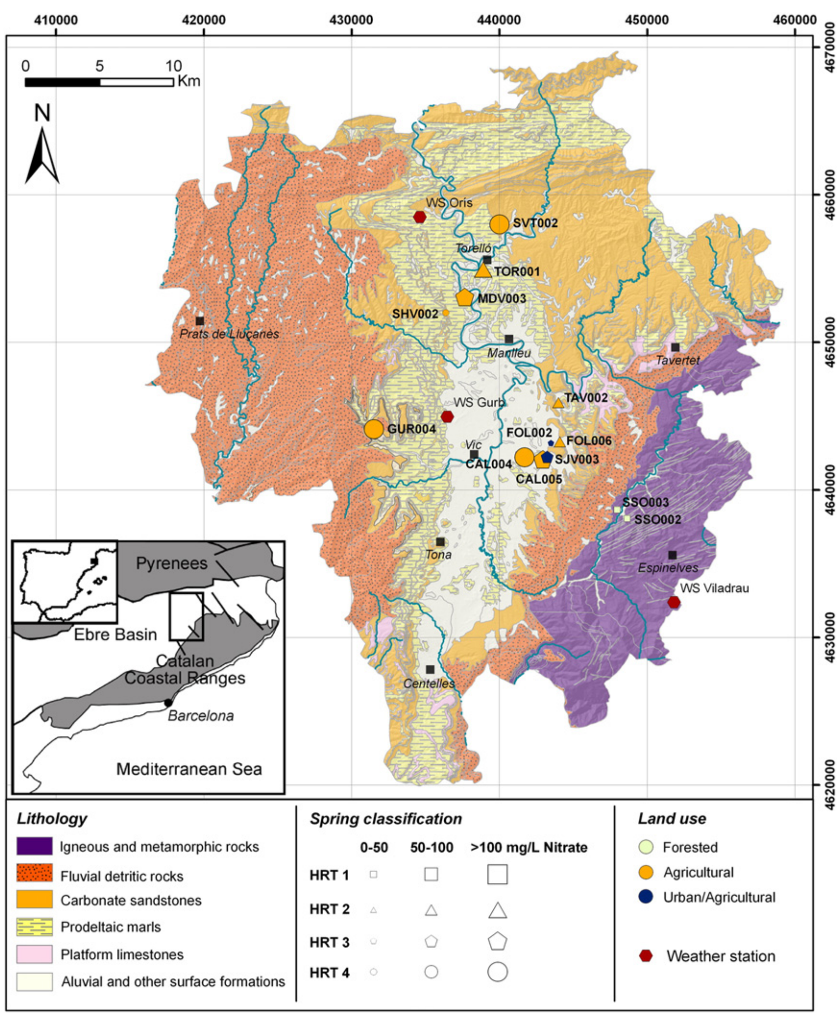


**Fig. 1.** Map of the geographical and geological setting of springs and the study area, with the locations and characteristics of the springs. Hydrological Response Types (HRT) are described later in Section 4.2. Geological formations are mapped according to the main lithology in the area (geological cartography simplified from ICC, 2011). Land use indicates the main type in the recharge area of the springs. Weather stations are also represented here.