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Analysis of vulnerability factors that control nitrate occurrence in natural springs (Osona Region, NE Spain)

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ABSTRACT

Nitrate pollution is one of the main concerns of groundwater management in most of the world's agricultural areas. In the Osona region of NE Spain, high concentrations of nitrates have been reported in wells. This study uses the occurrence of this pollutant in natural springs as an indicator of the sub-surface dynamics of the water cycle and shows how groundwater quality is affected by crop fertilization, as an approach to determine the aquifer vulnerability.

Nitrate concentration and other hydrochemical parameters based on a biannual database are reported for approximately 80 springs for the period 2004–2009. The background concentration of nitrate is first determined to distinguish polluted areas from natural nitrate occurrence. A statistical treatment using logistic regression and ANOVA is then performed to identify the significance of the effect of vulnerability factors such as the geological setting of the springs, land use in recharge areas, sampling periods, and chemical parameters like pH and EC, on groundwater nitrate pollution.

The results of the analysis identify a threshold value of 7–8 mg NO_3^-/L for nitrate pollution in this area. Logistic regression and ANOVA results show that an increase in EC or a decrease in pH values is linked to the possibility of higher nitrate concentrations in springs. These analyses also show that nitrate pollution is more dependent on land use than the geological setting of springs or sampling periods. Indeed, the specific geological and soil features of the uppermost layers in their recharge areas do not contribute to the buffering of nitrate impacts on aquifers as measured in natural springs. Land use, and particularly fertilization practices, are major factors in groundwater vulnerability.

1. Introduction

Water management uses multi-scale approaches to describe entire hydrogeological systems and provide sound criteria to preserve the quality of water resources. Indicators of the extent of human impacts, and of the progress in actions taken to protect subsoil water quality, applied to the different components of the hydrologic cycle, will each contribute a partial description of the water dynamics. Observing the processes that take place in the upper layers of the soil helps to describe the evolution of introduced pollutants and, therefore, explain the effect of human pressures and their consequences on groundwater quality (Böhlke, 2002). Springs are observation points that integrate the response of these upper layers to such pressures. The monitoring of springs can express the vulnerability of a given area to a potential alteration of its groundwater resources (Leibundgut, 1998; Manga, 2001; Elhatip et al., 2003; Katz et al., 2009).

Nitrate pollution is one of the main concerns of groundwater management in most of the world's agricultural areas. This is especially true in Europe, where the Nitrate Directive (ND; Directive 91/767/EU) and, more recently, the Water Framework Directive (WFD; Directive 2000/60/EC) and the Groundwater Directive (GWD; Directive 2006/118/EC) consider nitrate pollution as one of the main threats to ground water quality, requiring urgent and intensive monitoring and a strong policy.

This study of nitrate pollution in springs supplements new information on the subsoil nitrate dynamics in a hydrogeological system, especially regarding the most superficial fluxes, before nitrate reaches the aquifer. Springs are thus valuable indicators of the sub-surface dynamics of the water cycle, as well as of the effect of fertilizer application on crops.

Examples of the usefulness of characterizing springs to understand nitrate pollution sources and dynamics are described by Katz et al. (2001), Katz (2004), Katz et al. (2004), Happell et al. (2006), and Toth and Katz (2006), all of whom used different tracers to determine groundwater transit times. Nitrate and other pollutant migrations have also been studied, and their occurrence described, in the Upper Floridian Aquifer. Similar studies have been carried out in other areas, such as

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those by Burg and Heaton (1998) and Amiel et al. (2010), who analyze nitrate pollution problems in different springs in Israel through the isotopic and chemical characterization of their waters. In karst systems of Iowa, Arkansas, and Illinois (USA), Rowden et al. (2001), Peterson et al. (2002) and Panno and Kelly (2004), respectively, studied the movement of nitrates, and in some cases pesticides, from their application to their detection in springs. Salgado et al. (2003) analyzed different spring waters in Spain to characterize the parameters which mainly affected the potability of water. Jones and Smart (2005) analyzed long-term records of nitrate concentrations in karst springs in England to investigate the effects of different factors, such as human activities and weather conditions, on nitrate in those springs. Perrin et al. (2006) analyzed chemical variations in karst springs in Switzerland under flooding conditions, also considering nitrate pollution as one of the factors to take into account. Hershey et al. (2010) classified the hydrochemical characteristics of springs within the Great Basin (USA) in two groups to identify local and regional groundwater systems. Most of these studies were realized in karst systems and used large springs as sampling points for the entire hydrogeological system.

However, much of the above-mentioned research was conducted in large-scale, mainly karst aquifers representing the behavior of entire hydrogeological systems. Less attention has been given to small, ephemeral springs that are common in superficial, unconsolidated rock formations (alluvial, colluvial, eluvial, and mass-wasting deposits) in semi-arid environments. These springs reflect the immediate effect of human pressures, mainly fertilization, on the uppermost layers of the subsoil and their response to infiltration and solute migration to the saturated zone.

The hydrological performance of such springs in response to fertilization has been characterized in the Osona region, in NE Spain, classified by local legislation and in accordance with the ND as vulnerable to nitrate pollution from agricultural sources. Different studies, such as those of Vitòria et al. (2008), Otero et al. (2009) and Menció et al. (2011) have analyzed nitrate occurrence, distribution, dynamics and natural attenuation from a local and regional hydrogeological perspective. Nitrate concentration in Osona wells ranged from 14 to 396 mg/L in surveys conducted between 2003 and 2006. The Osona region is located in the internal basins of Catalonia, approximately 60 km north of Barcelona (Fig. 1). It has an area of 1260 km^2 and a total population of 150,000 inhabitants. This is an intensive livestock production area, with 927 intensive piggeries, and more than 600,000 head of livestock. Manure generated by livestock production is spread as organic fertilizer on the 307.45 km^2 of the row crops (25% of the study area), most of them situated in the Plana de Vic, the flat central part of the study area where most of the agricultural activity occurs.

Due to its geological and geomorphological characteristics, there are numerous springs in Osona, forming an important part of the cultural and natural heritage of the region. The local authority (*Consell Comarcal d'Osona*), aware of nitrate pollution and its effects on these springs, began a monitoring program in 2004 to survey the concentration of nitrates in them. Two sampling surveys per year have been carried out since then.

The main hydrogeological system of the area consists of a sequence of Paleogene sedimentary layers, constituted by conglomerates and a later succession of carbonate formations, with alternating calcareous, marl and sandstone layers (Reguant, 1967; Gich, 1972; Busquets et al., 1979; IGME, 1983, 1994; and Abad, 2001). It lies over Hercynian crystalline rocks (igneous and metamorphic). Paleogene formations show a uniform 5–10° dipping angle towards the west, and present an antiform structure at the area's northern border. Additionally, quaternary sediments, such as alluvial, colluvial, eluvial, and mass-wasting deposits, acting as local aquifers, are related to the occurrence of springs (Fig. 1).

Hydrochemical characteristics of these aquifers were described by Menció et al. (2011) obtaining three groundwater types in the Plana de Vic area: the dominating calcium-bicarbonate type and, the calcium-sulfate and calcium–sodium chloride types mainly associated to pyrite oxidation and local pollution problems, respectively. Additionally, pyrite oxidation was linked to natural nitrate attenuation; and, high chloride concentrations, and thus high electrical conductivities (EC), observed in this area were proportional to manure applications.

Logistic regression (LR) is a statistical method that predicts the probability of occurrence of a binary pattern (for example, the presence or absence of nitrate pollution) and allows the use of quantitative (discrete and continuous) and qualitative variables as predictor parameters. LR has been used in several hydrogeological systems affected by nitrate pollution to determine which vulnerability factors are more likely to be linked to nitrate pollution. For instance, Nolan et al. (2002) analyzed which variables could best predict the presence of nitrate pollution in shallow and recently recharged groundwater and Liu et al. (2005) and Carbó et al. (2009) used LR to determine which well conditions were best able to predict nitrate pollution. Antonakos and Lambrakis (2007) analyzed different methods to assess aquifer vulnerability to nitrates, including LR.

The purpose of this research is to investigate the response to fertilization of springs located in superficial unconsolidated deposits, some of which are also related to groundwater flow in the underlying consolidated rock, with the goal of assessing the major vulnerability factors that affect their nitrate concentration. Springs are herein considered as representative of the uppermost groundwater flow paths, and therefore revealing of soil dynamics with respect to nitrate occurrence, attenuation, and further migration to aquifers. The springs surveyed have average discharge rates of five to eight orders of magnitude, in line with Meinzer's (1923) and Kresic and Stevanovic's (2010) classifications.

In this paper, the nitrate concentration in springs for the period 2004–2009 is reported and analyzed. The background concentration of nitrate is determined and a statistical treatment using logistic regression and ANOVA is performed to identify the significance of the effect of different vulnerability factors on nitrate pollution. Factors such as 1) the hydrogeological classification of springs, 2) land use in their recharge area, 3) sampling periods, and 4) chemical parameters such as pH and conductivity are examined for any correlation with the corresponding nitrate concentration. This detailed portrayal of spring vulnerability to pollution may provide objective data on which to base policy actions to preserve spring-water quality, prevent groundwater pollution and, in addition, secure the local natural heritage.

2. Spring classification

The hydrogeological classification proposed by Fetter (1994), plus the supplementary categorization of Kresic and Stevanovic (2010), have been adapted to group the springs of Osona into five main categories, based on intrinsic geological characteristics. This classification is summarized in Fig. 2 and Table 1, and includes: 1) springs in crystalline rocks, related to the Hercynian basement; 2) springs in regional faults; 3) springs in pre-quaternary sedimentary rocks, related to Paleogene sedimentary rock formations; 4) springs in quaternary sediments, associated with alluvial, colluvial, eluvial or mass-wasting deposits; and 5) springs that drain both pre-quaternary and quaternary formations.

The specific characteristics of these springs are considered to obtain a more detailed classification. For instance, for those located in pre-quaternary sedimentary rocks, we differentiate between springs that appear due to the presence of dissolution-related porosity in limestone layers (3a, in Fig. 2 and/or Table 1), fractures in marls or sandstones (3b1), or, simply, permeability variations inherent in the spatial heterogeneity/layering of sedimentary materials (3b2). When the distinction between these different origins was not possible, springs were classified in a third group 3b. In quaternary sediments, we identify whether there is a sedimentary (i.e., related to facies