Universitat de Girona

NITRATE GROUNDWATER POLLUTION AND AQUIFER VULNERABILITY: THE CASE OF THE OSONA REGION

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PROGRAMA DE DOCTORAT EN
CIÈNCIES EXPERIMENTALS I SOSTENIBILITAT

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Memòria presentada per optar al títol de doctora per la Universitat de Girona

Universitat de Girona

La memòria "Nitrate groundwater pollution and aquifer vulnerability: the case of the Osona region" ha estat realitzada per la Mercè Boy Roura per a l'obtenció de la Menció Internacional en el títol de Doctora, sota la direcció del Dr. Josep Mas-Pla i la Dra. Anna Menció, de l'Àrea de Geodinàmica Externa del Departament de Ciències Ambientals de la Universitat de Girona.

Dr. Josep Mas-Pla Dra. Anna Menció Domingo Mercè Boy Roura

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ABSTRACT

Non-point agricultural pollution is a major concern in water resources management around the world. Farming activities, among other land uses, have deteriorated the quality of aquifers by introducing large quantities of nutrients. Elevated concentrations of nitrates cause a variety of environmental problems such as degradation of aquatic ecosystems, and can also cause health-related issues.

The Osona region (1,260 km^2, NE Spain) is an intensive agricultural and livestock production area, where large amounts of organic fertilizer are produced and applied on the crops every year. Nitrate contents above 50 mg/L are commonly found, reaching up 450 mg/L in some of the sampled wells and springs. Therefore, Osona was declared as vulnerable to nitrate pollution from agricultural sources in accordance with the Nitrate Directive (91/676/EC).

The principal aim of this doctoral thesis is to study the occurrence of nitrate pollution in groundwater by monitoring springs and wells, focusing on its transport to the subsurface, and to assess aquifer vulnerability in Osona. Most of the studies conducted to describe nitrate occurrence use water samples from wells. In the effort to characterize nitrate dynamics, this dissertation explores the suitability of spring water as a potential indicator of shallow groundwater systems quality and to understand nitrate recharge processes to aquifers. However, one cannot overlook water wells, since they are an important source for drinking water supply. Statistical analyses and regression models are tested to identify which variables significantly influence nitrate content in groundwater, as well as to create vulnerability maps.

Up to 131 natural springs were classified according their geologic setting and land use, which determine discharge, water chemistry and, specifically, nitrate content. Logistic regression and ANOVA analyses showed that nitrate pollution is more dependent on land use than the geological setting of springs. Accordingly to this, land uses, and particularly fertilization practices, are major factors that control groundwater nitrate content.

In order to evaluate temporal nitrate input to the subsurface, 13 natural springs were sampled over one year. Springs were classified in four groups describing their hydrological response type (HRT), based on discharge, electrical conductivity (EC) and nitrate data. Results indicated that even though discharge and EC could be related to specific hydrogeological behaviors, nitrate content showed uniform values in most of the springs with only a minor influence from external factors, such as major rainfall events. Temporal variations on nitrate concentrations due to fertilization regimes were not clearly observed. Such evenness of nitrate outflow might

be attributed to a homogenization of the subsurface processes that determine nitrate infiltration after decades of intensive fertilization using pig manure and slurry. Geostatistical analysis using variograms provided an additional insight into the discharge and nitrate temporal pattern. 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. These results complement previous studies only based on data from wells, which found that temporal fluctuations in nitrate content in aquifers were attributed to flow regime alterations due to groundwater withdrawal.

Furthermore, nitrate data from wells, obtained in a sampling campaign in 2010, were integrated into a multiple linear regression (MLR) model together with several explanatory variables, representing nitrogen sources, transport and attenuation, to assess groundwater vulnerability. The MLR determined the factors that significantly influence nitrate pollution, which are: nitrogen load as manure, aquifer type, presence of well-drained and deep soils, irrigation and occurrence of denitrification processes. The model featured three methodological innovations: net nitrogen input was determined throughout the region using a simple mass balance approach and a newly available GIS tool; the model addressed vertical aquifer layering; and detailed aquifer chemistry at well locations was incorporated into the model by a principal component analysis (PCA), in order to obtain a composite variable for subsequent interpolation by kriging.

Vulnerability maps for unconfined, leaky and confined aquifers were developed according to the calibrated regression model and reflect local patterns of nitrogen sources and aquifer susceptibility characteristics. On the basis of this model, new scenarios can be drawn to evaluate the effect of alternative agricultural management practices on groundwater quality. They can also be used for protection, planning and management of groundwater resources.

Therefore, nitrate pollution in groundwater in Osona is a persistent and widespread problem, as observed in the field and as reflected in the vulnerability maps. Springs are valuable indicators of shallow groundwater systems quality and together with data from wells, allow characterizing nitrate occurrence and the hydrodynamics of the aquifer systems. Moreover, statistical and regression analyses permit identifying the most significant factors that influence nitrate pollution in groundwater. Finally, a decrease in nitrate content in groundwater is not expected in the immediate future, unless pressures on the environment and water resources, especially agricultural fertilization practices, reduce their intensity and extension.

RESUM

La contaminació per nitrats associada a fonts difuses és una limitació important en la gestió dels recursos hídrics arreu del món. Les activitats agrícoles, entre altres usos del sòl, han deteriorat la qualitat dels aqüífers degut a l'entrada en excés de nutrients. Concentracions elevades de nitrats són l'origen de diverses problemàtiques ambientals com la degradació dels ecosistemes aquàtics, i també poden ocasionar problemes de salut pública.

La comarca d'Osona (1.260 km^2, NE d'Espanya) és una zona de producció agrícola i ramadera intensiva, on anualment es produeixen i s'apliquen grans quantitats de fertilitzants orgànics als conreus. Concentracions de nitrats superiors a 50 mg/L són comunes, arribant a valors de fins a 450 mg/L en alguns dels pous i fonts mostrejats. Com a conseqüència, Osona ha estat declarada com a zona vulnerable a la contaminació per nitrats d'origen agrari, d'acord amb la Directiva de Nitrats (91/676/CE).

L'objectiu principal d'aquesta tesi doctoral és l'estudi de la contaminació per nitrats a les aigües subterrànies mitjançant el mostreig de fonts i pous, centrant-se en el seu transport al subsòl, així com en l'avaluació de la vulnerabilitat dels aqüífers a Osona. La majoria dels estudis realitzats per descriure la contaminació per nitrats utilitzen mostres d'aigua de pou. Amb el propòsit de caracteritzar la dinàmica dels nitrats, aquesta tesi estudia la idoneïtat de l'aigua de les fonts com a possible indicador de la qualitat dels aqüífers superficials i per entendre els processos de recàrrega dels nitrats al subsòl. No obstant això, s'ha de tenir en compte l'aigua dels pous, ja que són un recurs important de proveïment d'aigua potable. En aquest estudi, s'utilitza l'anàlisi estadística i models de regressió per identificar les variables que influeixen de manera significativa la concentració de nitrats a les aigües subterrànies, i també per la creació de mapes de vulnerabilitat.

Per a la caracterització dels nitrats a l'aigua de les fonts naturals, es van classificar un total de 131 fonts segons el seu context geològic i l'ús del sòl, els quals determinen el cabal, la química de l'aigua i, en concret, el contingut de nitrats. La regressió logística i l'anàlisi ANOVA mostren que la contaminació per nitrats depèn més de l'ús del sòl que de les característiques geològiques. Així doncs, els usos del sòl, i en concret les pràctiques de fertilització, són el factor principal que determina la concentració de nitrats a les aigües subterrànies.

Per tal d'avaluar temporalment l'entrada de nitrats a les aigües subterrànies, es van mostrejar 13 fonts durant més d'un any. Aquestes es van classificar en quatre grups que descriuen el seu tipus de resposta hidrològica (TRH), en base al seu cabal, conductivitat elèctrica (CE) i nitrats.

Els resultats indiquen que, tot i que el cabal i la CE poden relacionar-se amb comportaments hidrogeològics específics, el contingut de nitrat es manté uniforme en la majoria de les fonts, amb només fluctuacions menors degudes a factors externs, com episodis de precipitació intensa. D'altra banda, no es van observar variacions temporals de la concentració de nitrats a causa dels períodes de fertilització. Aquesta uniformitat del flux de sortida de nitrats es pot atribuir a una homogeneïtzació dels processos que tenen lloc al subsòl i que són els que determinen la infiltració de nitrat, després de dècades de fertilització intensiva utilitzant fems i purins. L'anàlisi geoestadística, utilitzant variogrames, proporciona informació complementària sobre el comportament temporal del cabal i dels nitrats. Suposant que les dades de les fonts són representatives de la lixiviació de nitrats cap a l'aqüífer subjacent, el contingut de nitrat que s'infiltra i recarrega els aqüífers poc profunds hauria de mostrar un valor constant al llarg del temps, amb només petites fluctuacions degudes a processos naturals. Aquests resultats complementen estudis anteriors basats únicament en dades de pous, els quals concloïen que les fluctuacions temporals del contingut de nitrats als aqüífers s'atribueixen a alteracions dels fluxos subterranis a causa del bombament de les aigües subterrànies.

Addicionalment, les dades de nitrat dels pous, obtingudes en un mostreig al 2010, es van integrar en un model de regressió lineal múltiple (RLM), juntament amb diverses variables explicatives que representen les fonts de nitrogen, el seu transport i atenuació, per tal d'avaluar la vulnerabilitat de les aigües subterrànies. La RLM va permetre determinar quins factors influeixen de manera significativa a la contaminació per nitrats, que són: la càrrega de nitrogen, el tipus d'aqüífer, la presència de sòls ben drenats i profunds, la irrigació i l'existència de processos de desnitrificació. El model inclou tres innovacions metodològiques: l'entrada neta de nitrogen es va calcular per tota la comarca utilitzant un balanç de masses i una eina SIG nova; el model té en compte l'estratificació vertical del sistema d'aqüífers; i les dades hidroquímiques de cada pou es van incorporar al model mitjançant una anàlisi de components principals (PCA), per tal d'obtenir una variable que les integrés per la seva posterior interpolació per mètodes de kriging.

En base als resultats de la RLM, es van desenvolupar mapes de vulnerabilitat per aqüífers lliures, semi-confinats i confinats a partir de la calibració del model de regressió. Aquests mapes reflecteixen patrons locals de fonts de nitrogen i de les característiques de susceptibilitat de l'aqüífer. Aquest model permet avaluar nous escenaris, com per exemple l'efecte de pràctiques agrícoles alternatives sobre la qualitat de l'aigua subterrània. També es poden utilitzar per a la protecció, planificació i gestió de les aigües subterrànies.

En conclusió, la contaminació per nitrats de les aigües subterrànies a la comarca d'Osona és un problema persistent i generalitzat, tal i com s'observa al camp i als mapes de vulnerabilitat. Les fonts són bons indicadors de la qualitat dels aqüífers superficials , i juntament amb les dades de pous, permeten caracteritzar la contaminació per nitrats i la hidrodinàmica dels aqüífers. D'altra banda, l'anàlisi estadística i de regressió permet identificar els factors més importants que influeixen en la contaminació per nitrats de les aigües subterrànies. Finalment, no s'espera una disminució del contingut de nitrats en les aigües subterrànies en un futur immediat, llevat que la pressió sobre els recursos hídrics i el medi, i especialment les pràctiques de fertilització, redueixin la seva intensitat i extensió.

RESUMEN

La contaminación por nitratos asociada a fuentes difusas es una limitación importante en la gestión de los recursos hídricos en todo el mundo. Las actividades agrícolas, entre otros usos del suelo, han deteriorado la calidad de los acuíferos debido a la introducción en exceso de nutrientes. Concentraciones elevadas de nitrato son el origen de distintas problemáticas ambientales como la degradación de los ecosistemas acuáticos, y también pueden causar problemas de salud pública.

La comarca de Osona (1.260 km^2, NE de España) es una zona de producción agrícola y ganadera intensiva, donde anualmente se producen y se aplican grandes cantidades de fertilizantes orgánicos en los cultivos. Concentraciones de nitrato superiores a 50 mg/L son habituales, alcanzando valores de 450 mg/L en alguno de los pozos y manantiales muestreados. En consecuencia, Osona ha sido declarada zona vulnerable a la contaminación por nitratos de origen agrario, de acuerdo con la Directiva de Nitratos (91/676/CE).

El objetivo principal de esta tesis doctoral es el estudio de la contaminación por nitratos en las aguas subterráneas mediante el monitoreo de manantiales y pozos, centrándose en su transporte hacia el subsuelo, así como en la evaluación de la vulnerabilidad de los acuíferos en Osona. La mayoría de los estudios realizados para describir la contaminación por nitratos utilizan muestras de agua de pozo. Con el propósito de caracterizar la dinámica de los nitratos, esta tesis estudia la idoneidad del agua de los manantiales como posible indicador de la calidad de los acuíferos superficiales y para entender los procesos de recarga de nitratos en las aguas subterráneas. Sin embargo, también se tiene que tener en cuenta los pozos de agua, ya que constituyen una fuente importante de abastecimiento de agua potable. En este estudio, se utilizan análisis estadísticos y modelos de regresión para identificar las variables que influyen de manera significativa la concentración de nitratos y también para la creación de mapas de vulnerabilidad.

Para la caracterización de los nitratos en el agua de los manantiales, se clasificaron un total de 131 manantiales de acuerdo con su contexto geológico y usos del suelo, los cuales determinan el caudal, la química del agua y, en concreto, el contenido de nitrato. La regresión logística y el análisis ANOVA muestran que la contaminación por nitratos es más dependiente de los usos del suelo que de las características geológicas de los manantiales. Así pues, los usos del suelo, y en concreto las prácticas de fertilización, son el factor principal que determina la concentración de nitratos en las aguas subterráneas.

Con el fin de evaluar temporalmente la entrada de nitratos en el subsuelo, se muestrearon 13 manantiales durante más de un año. Éstos se clasificaron en cuatro grupos que describen su tipo de respuesta hidrológica (TRH), según su caudal, conductividad eléctrica (CE) y nitratos. Los resultados indican que a pesar de que el caudal y la CE pueden estar relacionados con comportamientos hidrogeológicos específicos, el contenido de nitrato muestra valores uniformes al largo del tiempo en la mayoría de manantiales, con sólo pequeñas influencias debidas a factores externos, como episodios de lluvia importantes. Por otra parte, no se observaron variaciones temporales en la concentración de nitratos a causa de los períodos de fertilización. Esta uniformidad del flujo de salida de nitratos se puede atribuir a la homogeneización de los procesos en el subsuelo que determinan la infiltración de nitrato, después de décadas de fertilización intensiva utilizando estiércol y purines. El análisis geoestadístico, utilizando variogramas, proporciona información complementaria sobre el comportamiento temporal del caudal y de los nitratos. Suponiendo que los datos de los manantiales son representativos de la lixiviación de nitrato hacia el acuífero subyacente, el contenido de nitrato que se infiltra y recarga los acuíferos poco profundos debería mostrar un valor constante en el tiempo, con sólo pequeñas fluctuaciones debidas a procesos naturales. Estos resultados complementan estudios anteriores basados únicamente en datos de pozos, los cuales concluyeron que las fluctuaciones temporales en el contenido de nitratos en los acuíferos eran atribuibles a alteraciones de los flujos subterráneos debido a la extracción de aguas subterráneas.

Además, los datos de nitrato de pozos, obtenidos en un muestreo en 2010, se integraron en un modelo de regresión lineal múltiple (RLM), junto con varias variables explicativas que representan las fuentes de nitrógeno, su transporte y atenuación, para evaluar la vulnerabilidad de las aguas subterráneas. La RLM determina los factores que influyen de forma significativa en la contaminación por nitratos, que son: la carga de nitrógeno, el tipo de acuífero, la presencia de suelos bien drenados y profundos, la irrigación y la existencia de procesos de desnitrificación. El modelo incluye tres innovaciones metodológicas: la entrada neta de nitrógeno fue calculada por toda la región utilizando un balance de masas y una herramienta SIG nueva; el modelo tiene en cuenta la estratificación vertical del sistema de acuíferos; y los datos hidroquímicos de cada pozo se incorporaron en el modelo mediante un análisis de componentes principales (PCA), para obtener una variable que las integrase para su posterior interpolación por métodos de kriging.

Basándonos en los resultados de la RLM, se han elaborado mapas de vulnerabilidad para acuíferos libres, semi-confinados y confinados a partir de la calibración del modelo de regresión. Estos mapas reflejan patrones locales de fuentes de nitrógeno y de las características de susceptibilidad del acuífero. Este modelo permite evaluar nuevos escenarios, como por ejemplo el efecto de prácticas agrícolas alternativas sobre la calidad del agua subterránea. También se pueden utilizar para la protección, planificación y gestión de las aguas subterráneas, y para la identificación de áreas susceptibles a la contaminación por nitratos.

En conclusión, la contaminación por nitratos de las aguas subterráneas en la comarca de Osona es un problema persistente y generalizado, tal y como se observa en el campo y en los mapas de vulnerabilidad. Los manantiales son buenos indicadores de la calidad de los acuíferos superficiales, y junto con los datos de pozos, permiten caracterizar la contaminación por nitratos y la hidrodinámica de los acuíferos. Por otra parte, el análisis estadístico y de regresión permite identificar los factores más importantes que influyen en la contaminación por nitratos. Por último, no se espera una disminución del contenido de nitratos en las aguas subterráneas en un futuro inmediato, a menos que la presión sobre los recursos hídricos y el medio, y especialmente las prácticas de fertilización, reduzcan su intensidad y extensión.

LIST OF PUBLICATIONS

List of publications in peer-reviewed journals derived from this doctoral thesis:

1. Menció, A., Boy, M., Mas-Pla, J., 2011. Analysis of vulnerability factors that control nitrate occurrence in natural springs (Osona region, NE Spain). *Science of the Total Environment* 409, 3049-3058.

   Impact factor: 3.258 (2012)
   Quartile and category: Q1 (31/209), Environmental Sciences

2. Boy-Roura, M., Menció, A., Mas-Pla, J., 2013. Temporal analysis of spring water data to assess nitrate inputs to groundwater in an agricultural area (Osona, NE Spain). Science of the Total Environment 452-453, 433-445.

   Impact factor: 3.258 (2012)
   Quartile and category: Q1 (31/209), Environmental Sciences

3. Boy-Roura, M., Nolan B.T., Menció A. and Mas-Pla J. Regression model for aquifer vulnerability assessment of nitrate pollution in the Osona region (NE Spain). Submitted to *Journal of Hydrology* in June 2013.

   Impact factor: 2.964 (2012)
   Quartile and category: Q1 (5/80) Water Resources; Q1 (4/122), Civil Engineering

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CHAPTER 1

General Introduction

1.1 – THE STATE OF THE WATER RESOURCES

Water resources, irregularly distributed in space and time, are under pressure due to the combination of both naturally occurring conditions and anthropogenic actions. The need to develop more sustainable practices for the management and efficient use of water resources, as well as the need to protect environmental ecosystems where these resources are located, has led to major shifts in awareness and public concern over the past years. However, economic convenience and political criteria are generally governing water resources development decisions at most local, regional, national and international levels, without taking into account environmental issues.

Population growth and rapid economic development have accelerated freshwater withdrawals. Water use shows high variability globally, both within sectors and across users (Figure 1.1).

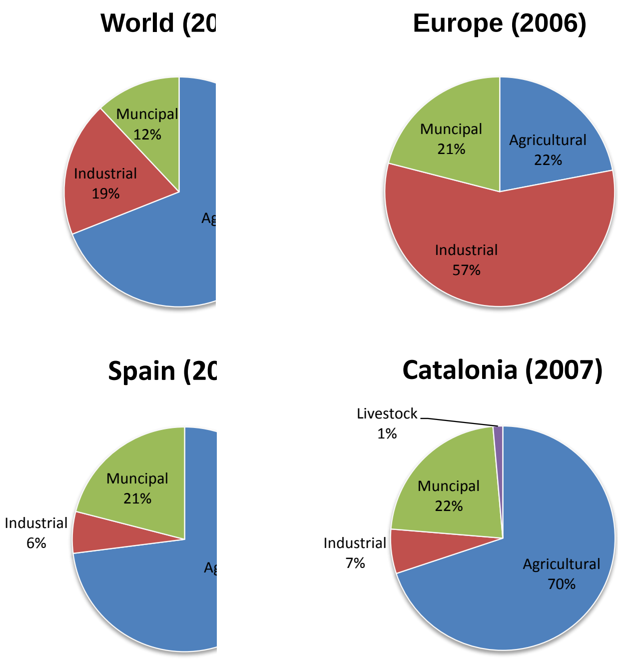


Figure 1.1 *– Water use by sector. Source: FAO, 2013; EEA, 2009; De Stefano and Llamas, 2013; ACA, 2007.*

The consumptive uses of freshwater from agriculture, industry and domestic sectors place the greatest pressures on natural systems, both in quantity and quality. In many countries of the world, agriculture is by far the main user of water. Irrigated agriculture accounts for about 70% of water withdrawals from available sources. After agriculture, the two major users of water are industry (19%), followed by domestic water supply (12%; FAO, 2013). In Europe, the industrial sector has a relevant importance and is the main consumer of water (57%) compared to agriculture use (22%; EEA, 2009). Nevertheless, in Spain and Catalonia, as well as in most arid and semiarid countries in the south of Europe, irrigation is again the main user of water due to the intensive agricultural activity with about 70% of the total water used (De Stefano and Llamas, 2013; ACA, 2010a).

About 92% of water uses (agricultural, industrial and municipal supply) are met by withdrawals from renewable sources, either surface water or groundwater. In areas of scarce freshwater resources, brackish water and wastewater are often used to meet water demand. Around 20% of the total water used globally is from groundwater sources, and about 74% is from surface water (FAO, 2013; Figure 1.2). Groundwater is the major source for drinking water, while surface water is for irrigation, energy and industry.

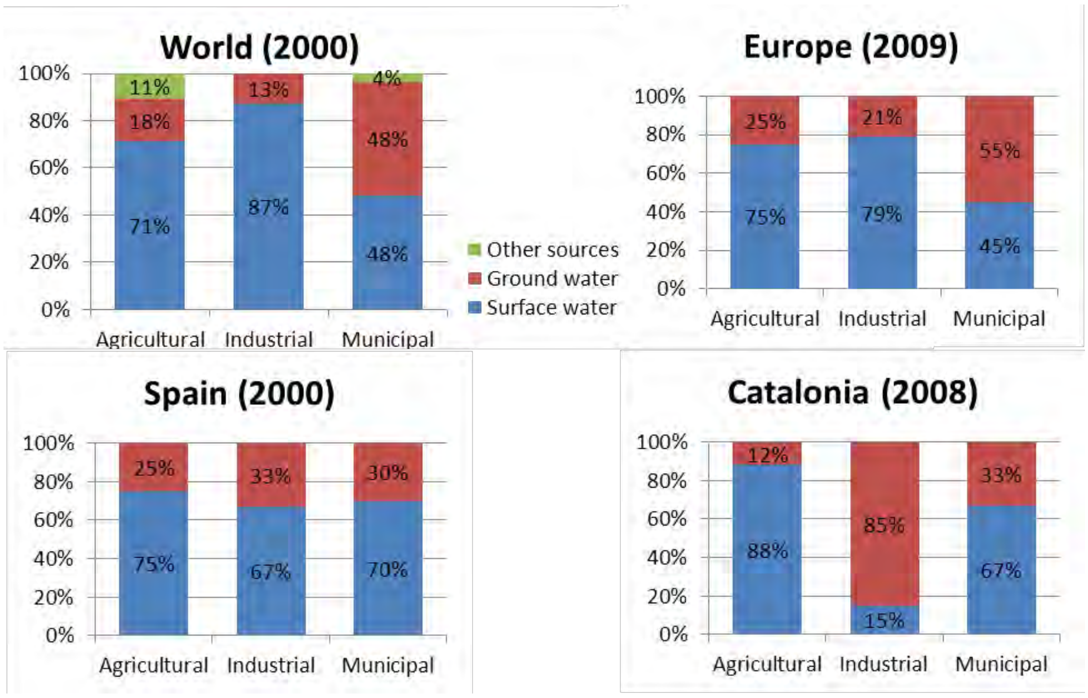


Figure 1.2 *– Water source by sector. Source: FAO, 2013; EEA, 2009; ACA, 2010b.*

Across Europe, surface water is the predominant source of freshwater, mainly because it can be abstracted easily, in large volumes and at relatively low cost. It therefore accounts for 81% of the total water abstracted and it is mainly used for industry and agriculture. Groundwater is the predominant source (about 55%) for public water supply due to its generally higher quality than surface water (EEA, 2009). In addition, in some locations it provides a more reliable supply than surface water in the summer months. In the case of Spain, surface water is widely used for all activities (about 70%; FAO, 2013). Groundwater irrigates about 25% of the total irrigated area. Increasing groundwater pumping allows farmers to guarantee their crops in drought years when surface water resources are not available. In Catalonia, surface water is the main source for agriculture and municipal supply (88% and 67%, respectively), although groundwater is generally used for industry (85%; ACA, 2010b). As competition among demand on water increases, there will be a need to improve water management and to create more efficient policies.

1.1.1 – Groundwater resources

The importance of groundwater is gaining recognition because this resource constitutes the predominant reservoir and strategic reserve of freshwater storage on the world. It represents 30 percent of the freshwater resources, and as much as 96 percent of the fraction in liquid form (WWAP, 2006, based on Shiklomanov and Rodda, 2003). Groundwater supplies more than 1.5 billion urban dwellers with water and it is extensively used for rural water supply. This resource is generally reliable in periods of droughts because of its large storage capacity. Moreover groundwater resources are cheap to obtain because of their widespread occurrence and they generally present good natural quality (Zaporezec, 2002).

Groundwater resources can, in many cases, supplement surface water, particularly as a source of drinking water. However, aquifers are often exploited at an unsustainable rate or affected by pollution. Protection of groundwater resources, both quantitatively and qualitatively, is becoming a more widespread global concern as typified by several new directives in the past decade. The quality of groundwater resources depends on a number of interrelated factors such as geology, climate, topography, biological processes and land use.

Groundwater is less vulnerable to anthropogenic impacts than surface water bodies, because it is naturally protected by the soil and underlying unsaturated zones or confining strata. However, as a result of large storage and long residence times when aquifers become polluted, contamination is persistent and difficult to reverse (Clarke et al., 1996). The compilation of aquifer vulnerability maps (this will be discussed more extensively later) provides land use managers with a valuable tool for the establishment of preventive and protective measures (Vrba and Zaporozec, 1994).

1.1.2 – Groundwater quality

Throughout the world, most countries' practices of urban and industrial development, agriculture and mining activities have caused groundwater contamination. Water quality is influenced by both direct point sources and non-point (diffuse) pollution. Diffuse pollution from farming activities and point source pollution from sewage treatment and industrial discharge are the principal contaminant sources. Concerning agriculture, the key pollutants include pesticides and organic fertilizers. The contaminants most commonly associated with manure are oxygen-demanding substances, ammonia, nutrients (particularly nitrogen and phosphorus), sediments, pathogens and odorous compounds. Manure is also a potential source of salts and trace metals, and to a lesser extent, antibiotics, pesticides and hormones. Hazardous chemicals and also oxygen-consuming substances are more related with point sources pollution.

One of the most common and persistent problem of groundwater pollution is associated with diffuse pollution generated through the intensification of agricultural practices over the last decades, with increased use of chemical fertilizers and higher concentrations of animals in smaller areas. Elevated concentrations of nutrients (especially nitrogen and phosphorus) can cause a variety of problems, including degradation of ecosystems, such as eutrophication of water bodies, and human health issues. Many factors affect the transport and concentrations of nutrients in groundwater, comprising the intensity and distribution of fertilizer and manure use, land management practices and other anthropogenic activities; as well as natural factors, such as soil and aquifer characteristics, hydrology, and the chemical properties of the nutrients compounds themselves.

Protection of groundwater sources is becoming a more widespread global concern as illustrated by the European Commission, which focuses on preventing rather than cleaning up pollution.

1.1.3 – Nitrate in groundwater

To better understand the nitrate problem, a general overview of the nitrogen cycle, nitrogen sources and factors involved in its transport are needed.

The nitrogen cycle

Groundwater nitrate is part of the global nitrogen cycle. Nitrogen is an essential element for all living organisms and, like other key elements, it flows through the environment in a dynamic cycle that supports organisms ranging from microbes to plants to animals. The natural nitrogen cycle is a balance between elemental nitrogen in the atmosphere and reactive forms of nitrogen moving through the soil-plant-animal-water-atmosphere cycle of ecosystems globally.

Nitrogen (N) represents the 78% of the atmosphere as elemental nitrogen (N_2). This form of nitrogen is inert and does not impact environmental quality since it is not bioavailable to most organisms. Nitrogen can form other compounds, however, which are bioavailable, mobile, and potentially harmful to the environment. The nitrogen cycle shows the various forms of nitrogen and the processes by which they are transformed and lost to the environment (Figure 1.3).

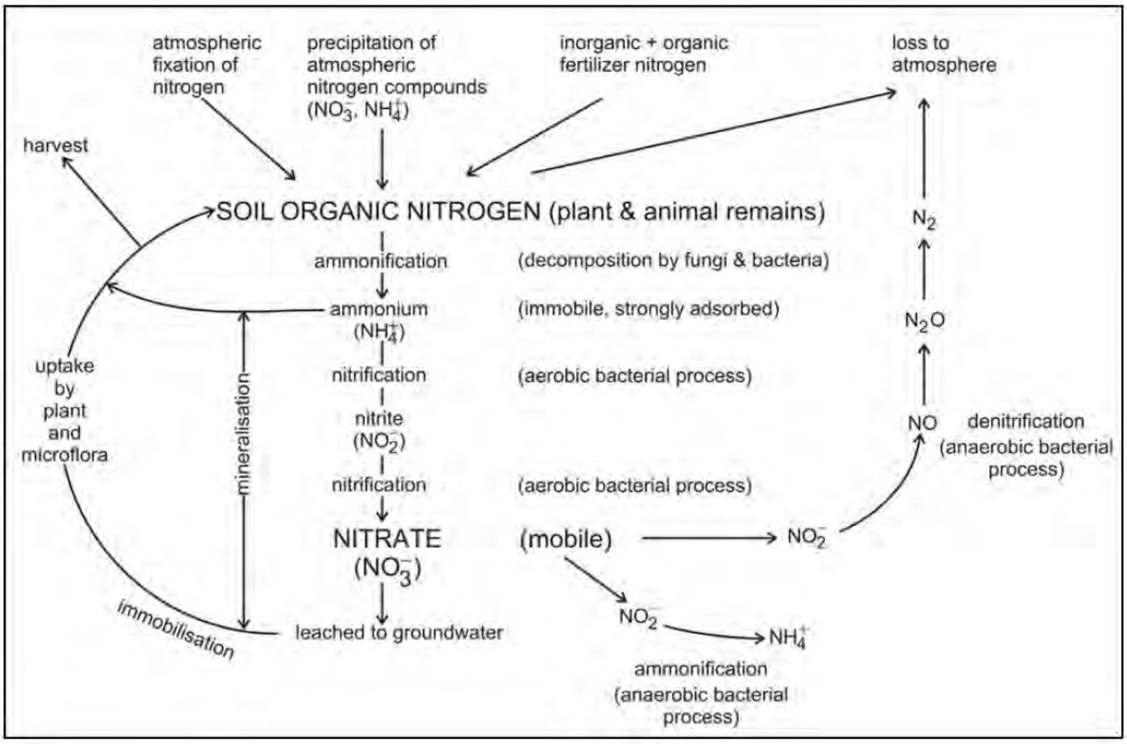


Figure 1.3 *– The biogeochemical nitrogen cycle. Source: Hiscock et al., 1991.*

Nitrogen in manure is primarily in the form of organic nitrogen and ammonia nitrogen compounds. In its organic form, nitrogen is unavailable to plants. Nonetheless, organic nitrogen (N_{org}) can be converted into inorganic forms through mineralization (Table 1.1). Mineralization takes places in different processes performed by soil microbes. The first product of this reaction is ammonium (NH_4^+). But in aerobic conditions, microbes can convert ammonium first to nitrite (NO_2^-) and then, the next step is oxidation to nitrate (NO_3^-), which is bioavailable and have fertilizer value. Plants assimilate nitrogen in the form of nitrate and ammonium. The nitrate assimilated is first reduced to ammonium, and then combined into organic forms.

Immobilization is the reverse process of mineralization, where ammonium and nitrate are taken up by soil organisms and plants and are converted into N_{org}. The ultimate fate of reactive nitrogen, which includes organic nitrogen, ammonium, nitrate, ammonia, nitrous oxide, etc., is to return back to the atmosphere as N_2. In the case of nitrate, this process is called denitrification and it is mediated by microbes in anoxic conditions. Another conversion of nitrite and ammonium to nitrogen gas (N_2) is triggered by a newly discovered bacterium called Annamox (Sutton et al., 2011).

Reaction	Formula	O_2 environment
Fixation	$N_2 \rightarrow N_{org}$	Aerobic
Mineralization	$N_{org} \rightarrow NH_3, NH_4^+$	Both
Nitrification	$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$	Aerobic
Immobilization	$NO_3^-, NH_4^+ \rightarrow N_{org}$	Aerobic
Denitrification	$NO_3^- \rightarrow NO_2^- \rightarrow N_2$	Anaerobic
Annamox reaction	$NO_2^-, NH_4^+ \rightarrow N_2$	Anaerobic

***Table 1.1** – Reactions involved in the nitrogen cycle. Source: modified from Sutton et al., 2011.*

Groundwater is becoming an important component of the global nitrogen cycle because of the increased nitrogen inflows and due to the long groundwater residence times. Nitrate does not significantly adhere or react with sediments or other geologic materials, and it moves with groundwater flow. In contrast, other forms of reactive nitrogen in groundwater are much less mobile and therefore less significant. For instance, ammonia occurs under some groundwater conditions, but it is subject to sorption and rapidly converts to nitrate under oxidizing conditions. Dissolved organic nitrogen (DON) concentrations are generally much lower than those of nitrate, due to the high adsorption of DON to aquifer materials.

Nitrogen can also enter the cycle from other sources such as natural, urban, industrial and agricultural sources. Nitrogen can be lost from the cycle through wells or via discharge to springs, streams and wetlands. Discharge to surface water sometimes involves denitrification or reduction of nitrate to ammonium when oxygen-depleted conditions exist beneath wetlands and in the soils immediately below streams (Harter et al., 2012).

Nitrogen sources in water

Sources of nitrogen in water can be divided according to their origin, whether they are naturally occurring or are human-induced sources.

a) Natural nitrogen sources

Nitrogen can be found naturally in groundwater, but at very low levels (<10 mg/L as NO_3; EEA, 1999). These concentrations that can be expected in the absence of significant human influence are named "background concentrations".

b) Anthropogenic nitrogen sources

The natural global nitrogen cycle has been extensively altered through human activities (Table 1.2), which have approximately doubled the rate of nitrogen (N) inputs into the terrestrial nitrogen cycle and have greatly increased the transfer of nitrogen from rivers to lakes and other sensitive receiving waters (Dubrovsky et al., 2010). Human-related sources of nutrients can be grouped into:

- **Point sources**: the position of the release point can be identified. These sources are normally regulated by laws that place limits on the types and amounts of contaminants that can be released to water.
- **Non-point (or diffuse) sources:** the local effect cannot be well tracked back to the source, or for which the source is characterized by a large geographical spread. Limiting nutrients from non-point sources is challenging because these sources are widespread and thus more difficult to identify and quantify than point sources.

	Natural	Agricultural	Industrial	Municipal
Diffuse sources	• Dissolution of minerals from soil or geologic formations • N atmospheric deposition • N-rich effluent discharge from groundwater baseflow to rivers	• Use of chemical N fertilizers • Use of organic fertilizers • Sludge spreading	• Atmospheric emissions from energy production • Combustion of fossil fuels	• Combustion engines in vehicles • Application of chemical fertilizers on residential lands
Point sources	• N-rich effluent discharge from springs to rivers	• Concentrated animals feeding operations (CAFO's) • Leaking slurry or manure tanks • Accidental spills of nitrogen-rich compounds	• Disposal of N-rich wastes • Leaching from landfills	• Septic tanks • Leaking sewerage systems • Leaching from landfills

***Table 1.2** – Types of nitrogen (N) sources. Source: modified from EEA, 1999.*

Nutrient transport to water

Nutrients released into the environment, either derived from point source or diffuse pollution, can be transported to streams in runoff from precipitation or irrigated fields, with inflowing groundwater, or through drainage ditches and subsurface tile-drain systems. Nutrients are also transported to groundwater by infiltrating rainfall or irrigation, which provide sources of water for recharge, and are released to the atmosphere by volatilization (Figure 1.4).

Within each of the hydrological compartments, nutrient concentrations are affected by physical factors, such as soil type, geology and slope of the land, and also by biological and geochemical processes that can change the chemical form of the nutrient and (or) transfer it from a compartment to another one. Environmental settings features determine the intensity in which chemical, physical and biological processes influence nutrient transport.

Assessment of the occurrence and transport of nutrients in water requires acknowledgment of complex interconnections among different variables that can affect the amount and timing of transport of nutrients to streams and groundwater. Human factors and actions that can affect transport include irrigation, groundwater pumping, presence of impermeable surfaces, artificial subsurface drainage, and best management practices. Those aspects will determine nutrients concentrations in water, even in watersheds that may have similar land uses and rates of fertilizer use.

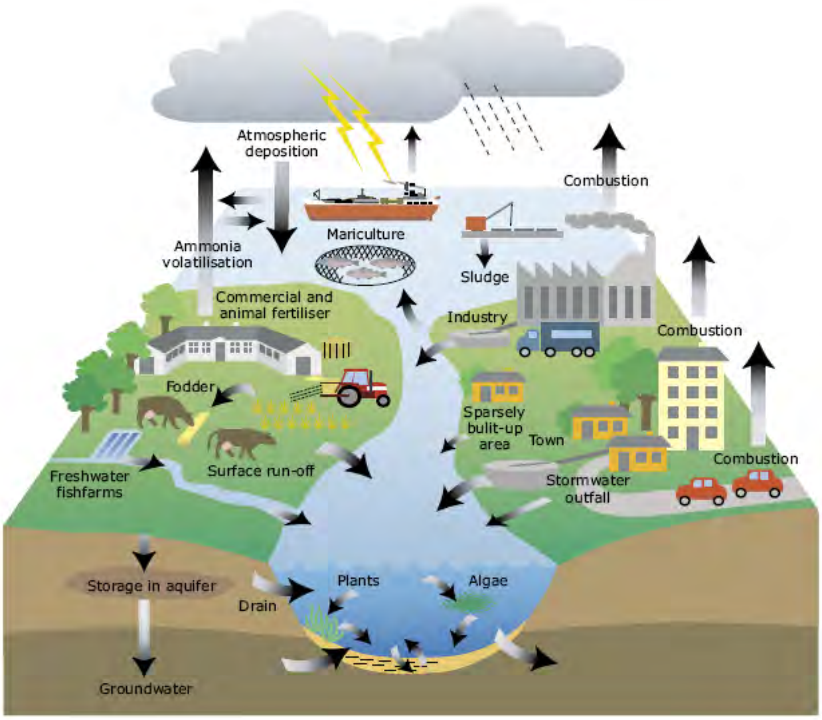


Figure 1.4 *– Water cycle and sources of nitrogen pollution. Source: Danish EPA, 2000.*

Chemical characteristics of the nutrients themselves are also important on nutrient transport because can affect mobility and persistence. Groundwater transport of nutrients is different from that in streams because only dissolved forms of nutrients can move substantial distances in groundwater. For example, nitrate readily dissolves and moves with water, and is not held on soil particles. Therefore, it is often the dominant nutrient species and is vulnerable to being washed out of the soil and infiltrated to groundwater. However, phosphorus attaches to soil particles and aquifer materials rather than dissolve.

Nutrient transport in water also depends on geochemical conditions of the water, which can affect the persistence of the contaminant. For instance, on one hand, when dissolved oxygen is present in groundwater and organic carbon content is low, nitrate is generally stable and therefore, persistent in groundwater. On the other hand, if dissolved oxygen is depleted and organic carbon is available, nitrate becomes unstable and is converted to nitrogen gas by bacteria in a redox reaction called denitrification.

Moreover, transport of nutrients to and within groundwater is less predictable than in streams due to groundwater flow is slower and more complex than the flow of streams. Intrinsic characteristics of aquifer systems also determine nutrient transport. Nitrate generally moves relatively slowly in soil and groundwater, and therefore there is a significant time lag between the polluting activity and the detection of the pollutant in groundwater (typically between 1 and 20 years, depending on the situation). The rate at which nitrate moves through an aquifer depends on the permeability and extent of fissuring in the aquifer, which controls flow, diffusion and dispersion processes. The recharge rate of an aquifer is another factor that influences groundwater flow regime and hence the movement of nitrate. For instance, nitrate can easily be transported to shallow groundwater in well-drained areas with rapid infiltration and highly permeable subsurface materials.

Alluvial and shallow aquifers are thus particularly vulnerable to nitrate pollution, while deep or confined aquifers are generally better protected. Surface or near-surface outcrops of confined aquifers, however, can allow nitrate to migrate towards deeper strata. Deep aquifers usually present lower nutrient concentrations because it takes a long time for water to move from the surface to deep layers (decades or even more in some cases), resulting in long residence times for groundwater and any solutes. These long travel distances increase the probability that nutrients will react. Protective low-permeability deposits may be also present between the land surface and deep aquifers, which hinder flow and transport of solutes to reach deep layers. Mixing of water from complex flow paths over long distances and time periods tends to result in a mixture of land-use influences on the deep groundwater quality, including contributions of nutrients from areas of undeveloped lands where concentrations are generally lower than those from developed lands. Nonetheless, it is important to note that groundwater at all depths is part of an integrated and interconnected hydrological system and is subject to contamination as water moves downward from the land surface. In this sense, future contamination of deep aquifers could pose serious concerns as these resources are commonly used for public water supplies, and restoration of this relatively inaccessible and slow-moving water would be costly and difficult (Dubrovsky et al., 2010).

Nitrate concentrations in groundwater may as well fluctuate according to seasonal and annual hydrological conditions.

Other factors that control nutrient transport are crop-management practices, which can accelerate infiltration of water and nutrients into the ground. Increases in nitrate leaching and run-off to groundwater and surface water can occur in agricultural areas where the soil layer is relatively thin or has poor nutrient buffering capacity. It can also happen where there are changes in land use, soil is bare of vegetation between crop rotation, and clearing of natural vegetation, which naturally have low rates of nitrate leaching (Addiscott et al., 1991). The intensification of agricultural activities has often resulted in significant overfertilization of crops to ensure maximum productivity. The problem comes when some fertilizer is not taken up by the crop, and when this exceeds the soil's buffering capacity, nitrate is leached from the soil into the groundwater. Moreover, irrigation, as well as drainage systems, can create downward flow of water from the root zone to the groundwater, thus transporting fertilizers.

Groundwater pumping also increases the flow of water and transport contaminant towards the pumped wells. Poorly designed wells can also allow nitrate pollution to move rapidly downwards by connecting shallow, polluted layers to deeper, non (or less) polluted layers.

Groundwater nitrate occurrence

Nitrate is among the most frequently detected contaminants in groundwater systems around the world (Spalding and Exner, 1993). In Europe, nitrate pollution is a major threat for water resources (EEA, 2012). Agriculture is the primary source of this nitrate, deriving from the input of chemical and organic fertilizers and subsequent leaching to groundwater. Public water supplies are largely below the World Health Organization guideline of 50 mg/L as nitrate (WHO, 2008); nonetheless, in some countries, private wells in rural areas have elevated nitrate concentrations reaching 10-15 times the recommended level.

Groundwater nitrate concentrations in Europe already increased during and after the World War II, as agriculture was gradually modernized and farming practices became much more intensive. The application of artificial nitrogenous fertilizers to crops began to increase significantly in the 1950s. Consequently, the amount of nitrate leached to groundwater increased and, eventually a gradual but marked raise in the concentration of nitrate in groundwater became evident in the early 1970s (EEA, 1999). Modern-day agricultural practices often require the intense use of fertilizers, leading to high nutrient surpluses that are transferred to groundwater and surface water. Nowadays, agricultural inputs of nitrate are still significant and need more attention to achieve good quality of water bodies. Improvement in nitrate groundwater quality will take time due to long transport processes in soils and groundwater and the slow renewal rate. Therefore, several years will be needed to see the results of all measures implanted by Member States to reduce nitrate pollution (EEA, 2012).

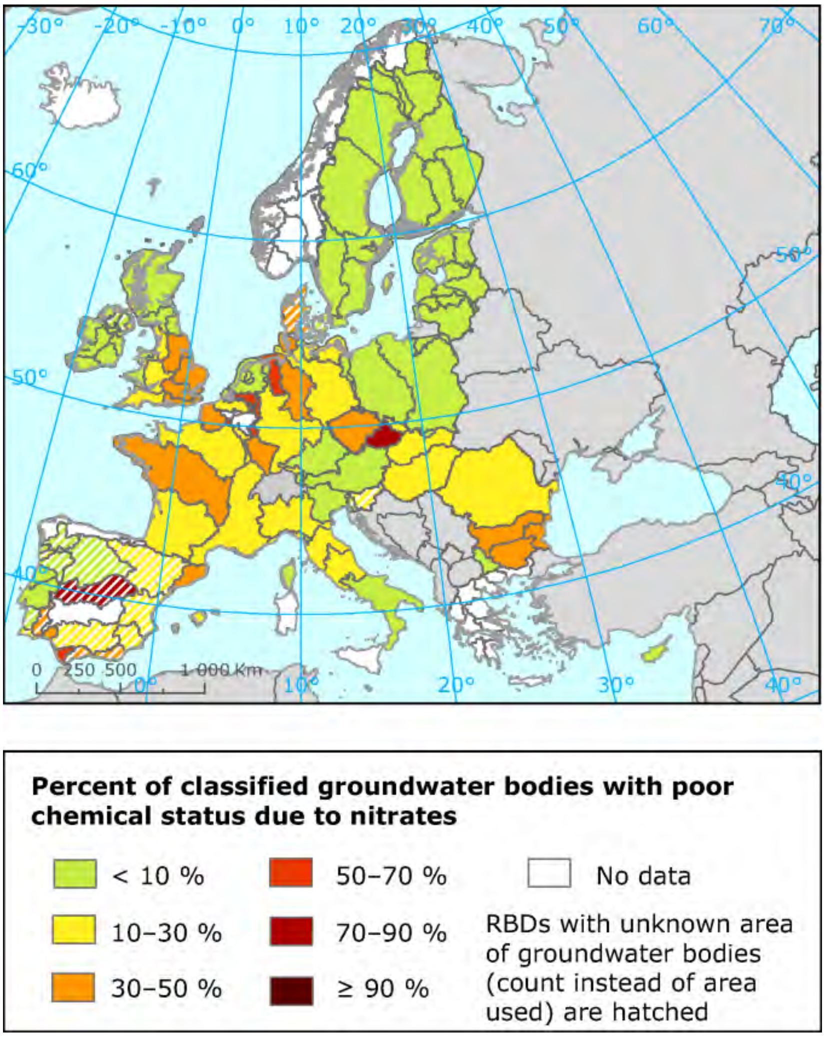


Figure 1.5 *– Percent of European groundwater bodies with poor chemical quality due to nitrates. Source: EEA, 2012.*

Mean nitrate concentrations in groundwater in Europe are above background levels (<10 mg/L as nitrate) but do not exceed 50 mg NO_3^-/L (EEA, 1999). As stated by the EEA in 2012, in 54% of the groundwater bodies in Europe that had poor chemical status, excessive nitrate concentration was responsible (Figure 1.5). The European Commission's report for the period 2004-2007 revealed that 15% of groundwater monitoring stations in the Member States found nitrate levels above 50 mg/L. On the other hand, 66% stations reported levels below 25 mg/L. However, nitrate concentrations are very different depending on the fertilizer consumption and the usage per hectare of agricultural land in each country. The Nordic countries have mean nitrate concentration below 2 mg NO_3^-/L, while in Western Europe mean nitrate content is above 25 mg NO_3^-/L. The most affected European countries by nitrate pollution in groundwater are Spain, France, Belgium, The Netherlands, Germany, Denmark, UK, Czech Republic and Bulgaria.

An indicator on the nitrogen balance indicates that there is a large nitrogen surplus in the agricultural soils of EU countries that can potentially pollute groundwater. Moreover, a high potential for nitrogen pollution in Western Europe results from the combination of high percentage of agricultural land and a high livestock density.

Excessive levels of nitrate are the most frequent cause of poor groundwater chemical status also in Spain, affecting 75% of the groundwater out of 297 groundwater bodies currently in poor quality status. The use of chemicals in agriculture and livestock rearing does not differ from other European countries, although the inherent climate and soil conditions of Spain explain the differences in terms of applications rates and types of fertilizers used. In some hot spots in Spain, more than 500 mg NO_3^-/L are found in groundwater in areas intensively irrigated with local groundwater where nitrate has been progressively accumulating in the aquifer. Nitrate reduction in the ground is a rare circumstance in most Spanish aquifers (De Stefano and Llamas, 2013).

The most deteriorated aquifers in Spain due to nitrate pollution are along the Mediterranean coast, especially in the Maresme region (Barcelona) with concentration up to 500 mg NO_3^-/L (Figure 1.6), and in the large plains in Castelló and València, as well as in Andalucía and in the archipelago of Canarias where nitrate concentrations are over 100 mg/L. Inland, in the plain of Castilla la Mancha, the alluvial aquifer of the Ebro river and some areas of the Guadalquivir valley are the most affected by nitrate pollution, where nitrate concentration range from 50 to 100 mg/L (IGME, 2009).

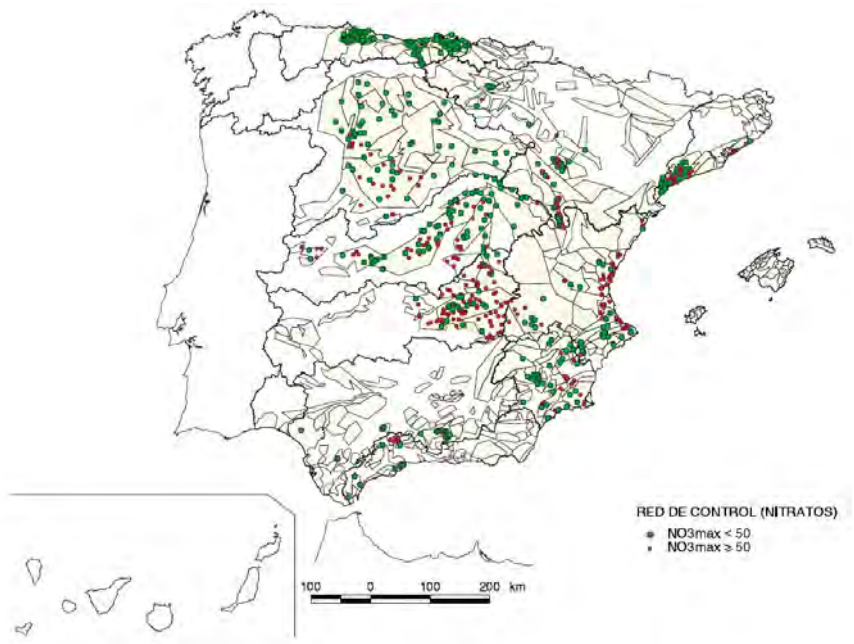


Figure 1.6 *– Map of Spain with groundwater quality monitoring sites with occurrence of nitrate. Source: Libro Blanco del Agua en España, MMA, 2000.*

Occurrence of nitrogen compounds is also the most important groundwater pollution problem from diffuse sources in Catalonia. A total of 17 out of 53 groundwater bodies are classified "at risk" to not accomplish the good quality status in 2015 required by the Water Directive Framework due to nitrate pollution (ACA, 2007).

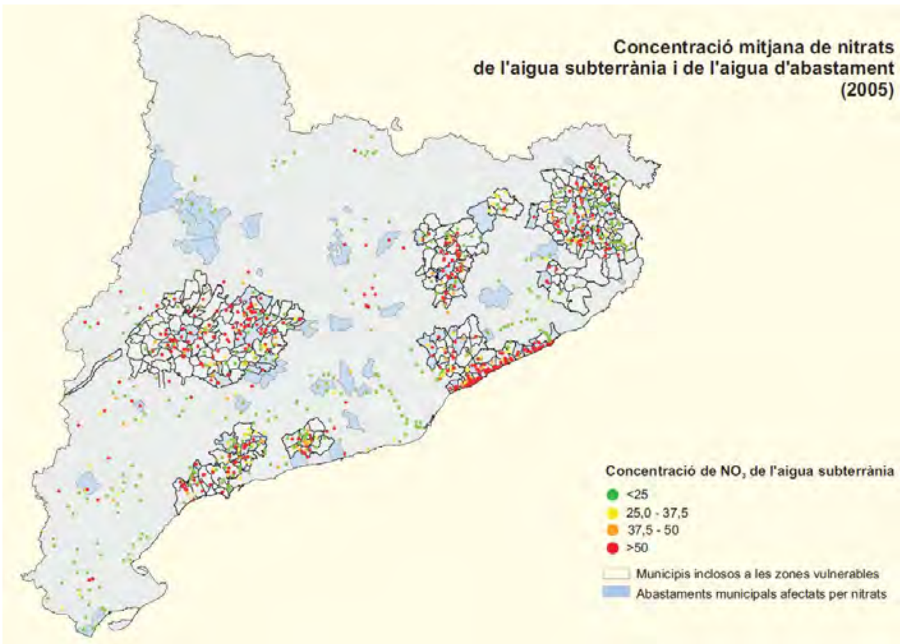


Figure 1.7 *– Mean nitrate concentrations in groundwater and in water public supply in Catalonia (2005). Source: ACA, 2007.*

About 45% of over 13,300 water samples analyzed by the Water Catalan Agency (ACA) have nitrate concentrations greater than 37.5 mg/L (Figure 1.7). According to the Health Department of the Catalan Government, 7% of the supply system in Catalonia has nitrate contents above 50 mg/L, mainly affecting small municipalities, representing less than 1.5% of the users in Catalonia. No significant variations in nitrate concentrations in groundwater have been observed for the period between 2001 and 2006, even though more variability is detected for higher nitrate values.

Problems associated with high levels of nitrate levels

Nitrate in groundwater has two major problems and risks. On one hand, nitrate pollution poses a recognized risk for its use as drinking water; while on the other hand, excessive nutrient loads can lead to the deterioration of ecosystems.

Health concern

High levels of nitrate in drinking water are associated with adverse health effects. In 1970, the World Health Organization (WHO) promulgated a guideline of 50 mg/L as nitrate in drinking water (equivalent to 11 mg/L as NO_3^--N; WHO, 2011a) and the U.S. Environmental Protection Agency (EPA) a maximum contaminant level (MCL) of 10 mg/L as NO_3^--N (equivalent to 45 mg/L as NO_3^-) to protect against methemoglobinemia in bottle-fed infants. This illness is also known as “blue baby syndrome”, a condition where inactivation of haemoglobin leads to a decrease in blood oxygenation carrying capacity, and to which infants are especially susceptible. Excess nitrate in drinking water may also pose risks for some types of cancer, and reproductive problems and congenital malformations (Ward et al., 2005; Ward and Brender, 2011).

In general, vegetables and meat are the main source of nitrate intake when nitrate levels in drinking water are below 10 mg/L. When nitrate levels in drinking water exceed 50 mg/L, then this will be the major source of total nitrate intake (WHO, 2011b). The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. In humans, about 25% of ingested nitrate is recirculated in saliva, of which about 20% is converted to nitrite by the action of bacteria in the mouth. Nitrite was shown to react with nitrosatable compounds in the human stomach to form N-nitroso compounds, which have been found to be carcinogenic.

Epidemiological studies on these links, however, still remain sparse to draw firm conclusions and there is considerable debate and a lack of consensus on the interpretation of medical evidence (van Grinsven et al., 2006; Ward et al., 2005).

Animals may also be affected by high nitrate concentrations in drinking water. The digestive system of ruminant animals (cows, sheep and goats) favor the transformation of nitrate to nitrite. Other non-ruminant animals (pigs and horses) are also sensitive and could suffer from methemoglobinemia.

Environmental concern

High levels of nitrate are also of environmental concern. Many aquifers discharge or are in hydraulic continuity with rives reaching coastal areas or surface water bodies as wetlands, where important nutrients loads can lead to eutrophication. Elevated nitrate concentrations may lead to excessive algal growth, which can cause oxygen deficiencies causing fish kills, toxic algal blooms and a general decrease in biodiversity (EEA, 1999).

Social concern

All these mentioned problems related to nitrate pollution have implied an organized concern about this potential health hazard among local citizens. Since the mid-80’s, agricultural pollution has become one of the most prominent environmental issues at the European Union and public opinion regards agriculture as one of the most environmentally disruptive social activities. As a result, the pressures on farmers to decrease pollution and achieve higher environmental standard were reinforced (Izcara et al., 2002). This transformation was in part the result of the implementation of different European directives regarding water quality, setting legal standards for a range of water quality parameters. The violation of the legal threshold for nitrates, in particular, increased the social concern of the problem of nitrate pollution. Several environmental organizations joined the cause worldwide accusing that claiming that nitrate pollution in groundwater exceeded safe-drinking water standards, mainly because dairies violate several environmental laws by applying manure to crops in excess.

Moreover, financial costs are also associated to poor water quality. Nitrate pollution in groundwater implies additional drinking water treatment, construction of new wells, monitoring and other safe drinking water actions.

Legal framework

As a consequence of the social movements and a growing public health concern, nitrate pollution control and regulation was set up on the policy agendas of European countries during the second half of the 1980's (Izcara et al., 2002). The **Nitrates Directive** (ND) 91/676/EC (EC, 1991), whose principal aim is to reduce and prevent water from pollution by nitrates from agricultural sources, is the most important directive regarding agriculture and water quality since it regulates the amount of manure applications (170 kg N/ha year).

The Nitrates Directive contains five main elements:

- Identification of polluted, or at risk of pollution, water bodies.
- Designation of "Nitrate Vulnerable Zones" (NVZs).
- Establishment of voluntary codes of good agricultural practices.
- Establishment of compulsory action programs within the NVZs.
- National monitoring of groundwater and surface water and reporting every 4 years.

The ND was transposed into Spanish legislation by the Real Decreto 261/1996. In Spain, a total of 57 NVZs have been declared, which cover about 13% of the national territory. In Catalonia, it was transposed by the Decret 283/1998 (updated by the Decret 476/2004 and Acord Gov/128/2009), which currently designates 12 NVZs, including 421 municipalities, covering up to 40 % of the total area. Almost 50% of the vulnerable areas have nitrate concentrations higher than 40 mg/L and there is not a clear trend of decreasing concentrations.

Several guides and manuals have been drawn up to improve manure management in order to reduce nitrate leaching to groundwater. Some examples are the "Code of good agricultural practices" (DARP, 2000) following Nitrate Directive or the "Guide to the treatment of livestock manure" (CADS, 2008), which help farmers to minimize the production of manure and slurry (livestock' diets, use of water in farms…) and give recommendations on when and how to apply organic fertilizer depending on seasonal crop requirements.

The European Commission's report for the period 2004-2007 revealed that nitrate concentrations in surface water remained stable or fell at 70% of monitored sites. Meanwhile, quality at 66% of groundwater monitoring points was stable or improved (EU, 2010).

Reducing nitrate is an integral part of the **Water Framework Directive** (WFD) 2000/60/EC (EC, 2000), which establishes a comprehensive, cross-border approach to water protection organized around river basin districts, with the aim of achieving a good status for European bodies of water by 2015. This Directive was transposed into Spanish legislation in 2003 by the modification of Ley 62/2003 and Ley de Aguas 1/2001.

The **Groundwater Directive** (GD) 2006/118/EC (EC, 2006) establishes a regime to assess groundwater chemical status, providing EU-wide quality standards for nitrate and pesticides, and requiring standards to be set at national level for a range of pollutants. This directive confirms that nitrate concentrations must not exceed the value of 50 mg/L, even though several Member States have set their own tighter limits in order to reach good quality status. The GD was transposed to Spanish legislation by the Real Decreto 1514/2009.

Achieving the objectives on water quality from European Directives poses technical and administrative coordination problems, as well as financial and political issues, because of the different authorities at national and regional levels. Several aquifers and the related springs and surface water bodies will not reach good status by 2015 (De Stefano and Llamas, 2013) as required by the WFD. This means that new terms will have to be negotiated and new strategies will need to be defined.

1.2 – A CASE STUDY: THE NITRATE PROBLEM IN THE OSONA REGION

1.2.1 – Geographical situation

The Osona region is located in the Barcelona province, in the central part of Catalonia, in the north-east of Spain (Figure 1.8). It has an area of 1,260 km^2 and a total population of 154,588 inhabitants in 2012. The capital of the region is the city of Vic. Osona is situated at the north-east corner of the Catalan Central Depression, between the Pre-Pyrenees, the Catalan Transversal Range and the Catalan Pre-Coastal Range.

Two main geographical units can be distinguished:

- **Plana de Vic** (Plain of Vic): it is a 30 km long and 15 km wide (450 km^2) depression located in the central part of the Osona region, stretching in a north-south direction. This natural depression is carved by the Ter River and its tributaries (Ges, Gurri, Sorreig and Congost streams). Its mean altitude is 500 m.a.s.l. and is completely surrounded by mountains: the Pre-Pyrenees in the north (with Serra de Bellmunt i de Curull mountain range with 1,246 m at the top), the Transversal range in the east (Collsacabra with 950 m), the Guilleries and the Montseny in the southeast (800 m-1,700 m), the Congost in the south (about 500 m) and the Lluçanès plateau in the west.

- **Lluçanès**: it is a high plateau about 400 km^2, transitioning between the Plana de Vic and the Berguedà region, in the Pre-Pyrenees. The major waterways of the area are tributaries to the Llobregat River (Lluçanès and Gavarresa streams).

Figure 1.8 *– Situation of the Osona region and its main geographical units.*

1.2.2 – Geological setting

The geological system of the Osona region consists of a sequence of Paleogene sedimentary layers, with a total thickness of approximately 1,500 meters, which overlies the Paleozoic crystalline rock (igneous and metamorphic) basement. The stratigraphic sequence is constituted by a thick (≈500 m) basal level of conglomerates and a later alternation of carbonate formations with calcareous, marl and carbonate sandstone layers (Abad, 2001; IGME, 2006; Menció et al., 2011b; Figure 1.9 and 1.10). Marl strata are dominant in the central and western part of Plana de Vic, reaching a thickness of about 300 m. Some gypsum layers are also locally found in the south-west of Plana de Vic. These formations show a dipping to the west of about 5-10º that is quite uniform, and only have an antiform structure at the Bellmunt mountain range. However, significant variations in thickness and facies transitions are common in this sedimentary basin, as evidenced by signs of a strong structural influence in its evolution during the early Tertiary. Despite this structural control during the Paleogene, faults were not significantly active later on, and especially not during the Quaternary. Hence, the present morphological features of Plana de Vic basin are not defined by major structural elements, but are related to erosion processes controlled by the evolution of the Ter River and its drainage basin, profiting the abundance of silty marl layers in the central area. Quaternary sediments overlay the rocks mentioned above and support agricultural activity. In particular, the main alluvial formations are located in the central part of the basin and constitute local unconfined aquifers, especially in the Ter River terraces and its floodplain.

In detail, the main lithology and geological formation that are found in Osona are summarized as follows (Abad, 2001; IGME, 2006; Mas-Pla et al., 2006 and 2008):

- **Paleozoic rocks:** they are constituted by igneous and metamorphic rocks and are located in the south-west of the Osona region, in the mountain area of Montseny and Guilleries. Their hydrogeological potential is limited to the groundwater flux through the fractures, commonly with low permeability. This hydrogeological system is disconnected from the one in Plana de Vic.

- **Mesozoic rocks:** with a limited distribution to the southernmost part of the study area. They are constituted by limestone formations, and silt layers with gypsum. Hydrogeologically speaking, they become locally relevant when those carbonate layers are exploited as aquifers. Moreover, they can be hydraulically connected to the Paleogene formations present in Plana de Vic. Nevertheless, their influence on the hydrogeological system of the Osona region is not relevant in the framework of this thesis.

- **Paleogene rocks:** the stratigraphic sequence corresponding to the Paleogene consists in the sedimentary formation that filled the Tertiary basin before and during the Pyrenees formation during the Alpine orogeny. However, the Osona region acted as the “avant-pays” and did not suffered major tectonic deformation. Only in its northern part, associated to the southern thrusts of the Pyrenees range, it shows relevant deformation structures. Among them, it is worth mention the Bellmunt antiform, which acts as a recharge area of the eastern Osona hydrogeological system. Nevertheless, the Paleogen sedimentary sequence lies as a monoclonal structure with a west dipping.

  The following geological formations are found from bottom to top:

  - *Vilanova and Romagats Fms.:* they are constituted by silicic conglomerates and sandstones with a potential thickness of 225 m. They are found continuously in the eastern part of the study area, overlying the Paleozoic basement; and in the south of the Osona region, overlying the Mesozoic rocks.

- *Tavertet Fm.*: it consists in limestones and marly-limestones with a mean thickness of 35 m, even though it becomes thinner along Plana de Vic in the south-west direction. Its hydrogeological potential is substantial.

- *Banyoles Fm*.: marls and sandy-marls with a thickness of 120 m. However, this layer also turns thinner in the south-west direction, and it transitionally becomes the Folgueroles Fm., formed mainly by sandstones.

- *Bellmunt Fm*.: it is constituted by sandstones, conglomerates and silt. It is located in the northern part of Osona, associated to the Bellmunt antiform and has a thickness of hundreds of meters.

- *Folgueroles Fm*.: sandstones, conglomerates and silt are found in this formation. It is located in the eastern part of Osona. In the north, in Bellmunt mountain range, overlies the Banyoles Fm., and in the south, it overlies the Romagats Fm. Its thickness ranges from 50 to 200 m.

- *Lower deltaic complex:* it is a sedimentary unit that belongs to a deltaic system with a thickness of hundreds of meters. Two main units can be distinguished: the main, lower formation is mainly constituted by marls (Igualada Fm. and Guixa-Gurb marls Fm.), which in the north becomes Puigsacalm Fm. with dominance of sandstones; while the upper unit is characterized by deltaic platforms constituted by fine-grain sandstones and silt (Voltregà Fm.). In detail:

    - *Puigsacalm Fm*.: it consists in sandy-marls with calcareous components, which formed the mountain ranges of Bellmunt and Collsacabra. Its maximum thickness is about 900 m, even though it gets thinner in the south-west direction, when the marls of Igualada Fm. are present.

    - *Igualada Fm*.: this formation is also commonly known as "Marls of Vic". It has a relevant thickness of up to 600 m in the central part of the region which includes marls, marly-sandstones with intercalations of sandstones. In these layers, there is evidence of occurrence of pyrite in the marly sediments. Where sandstones dominate, it may actually present fracture porosity.

    - *Guixa-Gurb marls Fm.:* it is an important marls formation with evident fractures with dominance of fine sediments located in Plana de Vic. It reaches a maximum thickness of 150 m in the central part of Plana de Vic.

    - *Voltregà sandstones Fm.:* coarse-grain carbonate sandstones and eventually, microconglomerates. Its thickness varies with a prograding deltaic system with a maximum thickness of 150 m.

  - *Upper deltaic complex:* a second deltaic complex develops at the north-western part of the study area, in the Lluçanès plateau. It is formed by the following lithostratigraphic formations:

    - *Vespella Fm*.: marls, marly-sandstones and sandstones with predominance of fine-grain sediments. It is found in the western part of Plana de Vic/eastern part of Lluçanès, from north to south. Occurrence of pyrite is also found in this formation.

    - *St. Martí Xic sandstones*: they are constituted by a prograding body of sandstones and microconglomerates from the north as a result of the Pyrenees formation. Its thickness is variable and it may reach up to 300 m.

    - *Tossa Fm*.: small, discontinuous, reef-patch formed by limestones and carbonate-sandstones with a maximum thickness of 20 m.

  - *Cardona Fm.:* at the top of the sedimentary basin infilling, evaporitic rocks formed and generated important layers of gypsum and salt. Its occurrence is very limited in the study area, yet it constitutes an important evaporitic formation (the Catalan Potassic Basin) a few tens of kilometers west bound.

  - *Artés Fm.:* it is widely found in the Lluçanès area and it is constituted by sandstones and silt of fluvial origin. It shows a large and variable thickness that may reach more than hundred meters to the south-west.

- **Quaternary sediments:** this formation, together with other quaternary formations, such as colluvial, eluvial, and mass-wasting deposits, is mainly related to the drainage basin of the Ter River. Their extension is mainly limited to the central part of the Plana de Vic.

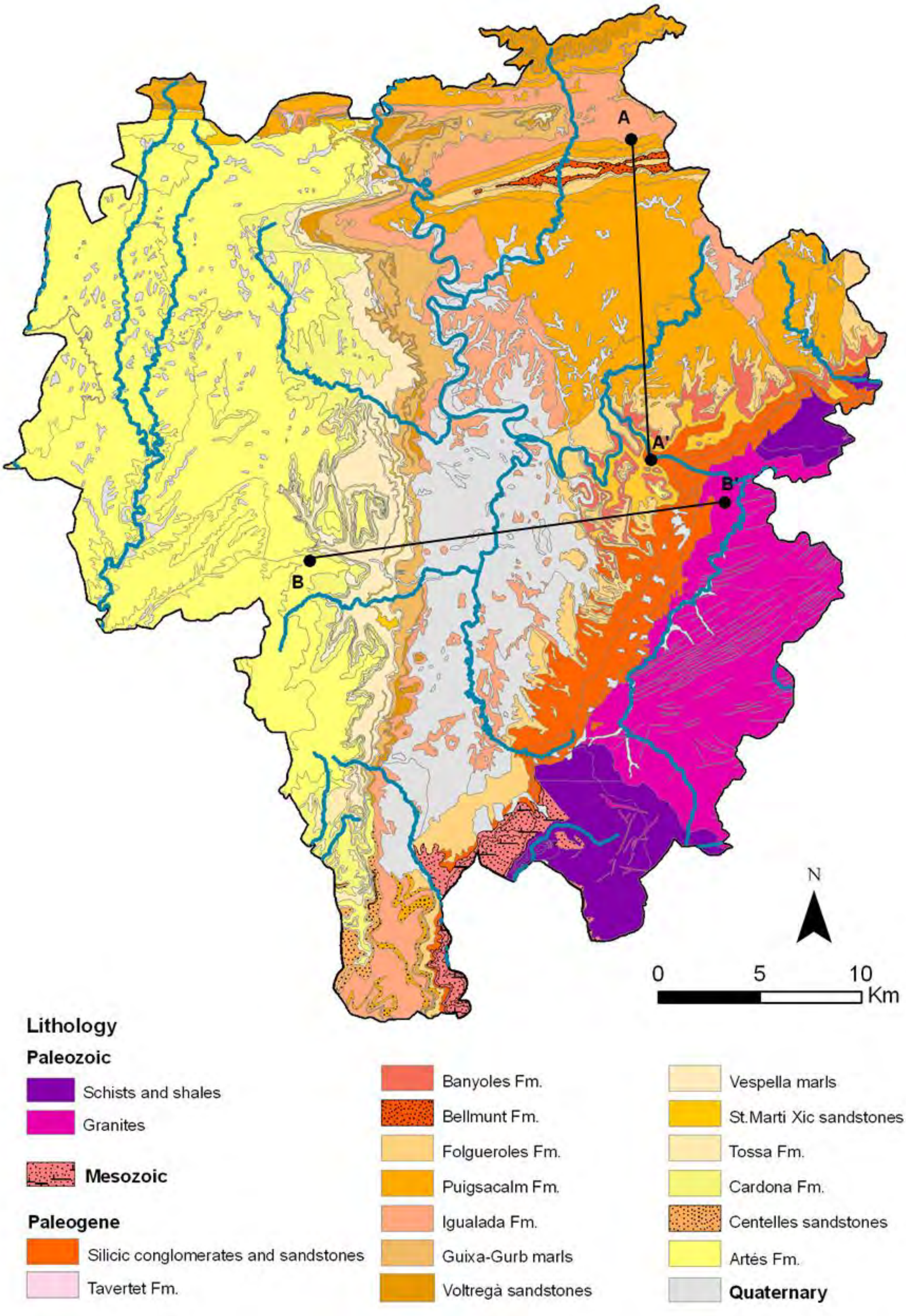


Figure 1.9 *– Geological map with the main lithologies and the location of the cross-sections representative of Plana de Vic (Figure 1.10).*

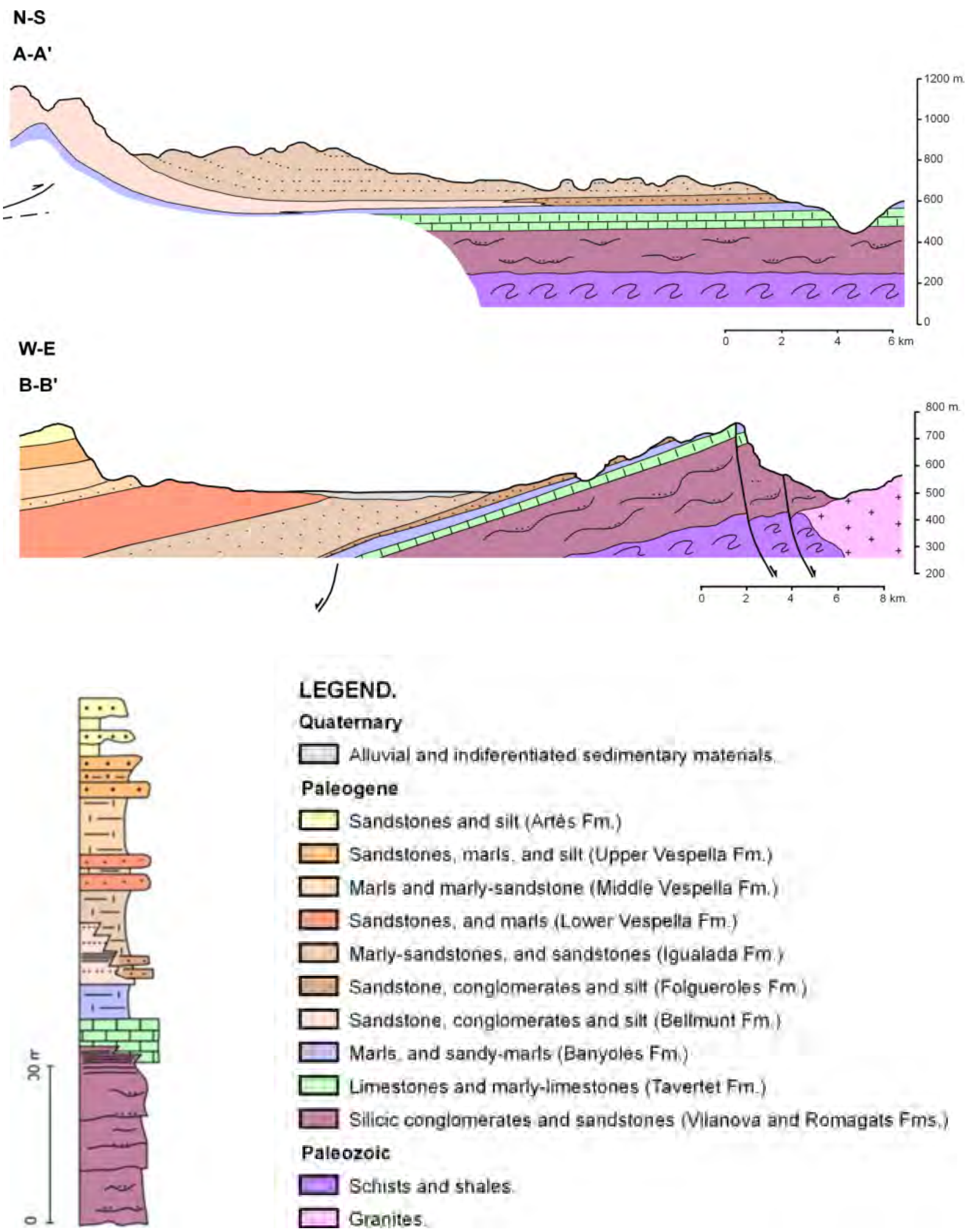


Figure 1.10 *– Stratigraphic column and geological cross-sections representative of Plana de Vic. Source: Menció et al., 2011b.*

1.2.3 – Hydrogeological setting

Hydrogeologically, the system consists of a series of aquifers located in carbonate and carbonate-sandstone layers whose porosity is mainly due to the fracture network of variable density, roughly oriented N-S and E-W throughout the study area, and occasionally due to dissolution. Fractures may eventually affect marls in specific areas, when their sand content is significant, and consequently act as aquitards, permitting a vertical leakage to the underlying leaky aquifers. Occasionally, marl layers act as aquicludes, and therefore as truly confining layers. Therefore, confined aquifers can also be found in the study area.

Shallow wells (<30 m deep) are located in the alluvial aquifers, while deeper wells usually reach 100 m depth, or even deeper, in search of the more productive aquifers exploiting the sandstone layers of the Folgueroles or Igualada Fms.

The main hydrogeological units that are distinguished as aquifers are:

- Paleogene units that present an intergranular porosity and later on, due to dissolution (Romagats and Folgueroles Fms.), or due to fractures and dissolution (Tavertet Fm. and occasionally Igualada Fm.).
- Quaternary sediments, especially alluvial sediments of the main rivers. Other quaternary formations, such as colluvial, eluvial, and mass-wasting deposits, also form potential small-scale hydrogeologic units.

Other formations have been defined as aquitards:

- Marl-sandy layers with predominance of fine sandy sediments developed in Igualada Fm. and occasionally in Vespella Fm. as well. The former constitute the multi-layered aquifer found in Plana de Vic. The later formation isolates the upper Artés Fm., with a considerable hydrogeological potential, from the layers found underneath. The hydrogeological potential of these Vespella Fm. marl layers is low, and it locally depends on their fracture network.

The potentiometric map of the Plana de Vic hydrogeological system with the main flow directions shows a westbound discharge system (Menció et al, 2011b; Figure 1.11). Potentiometric lines are based on shallow and deep wells, since no significant differences in groundwater level have been identified among them. This is due to the lack of well casing, which equals hydraulic head among different levels.

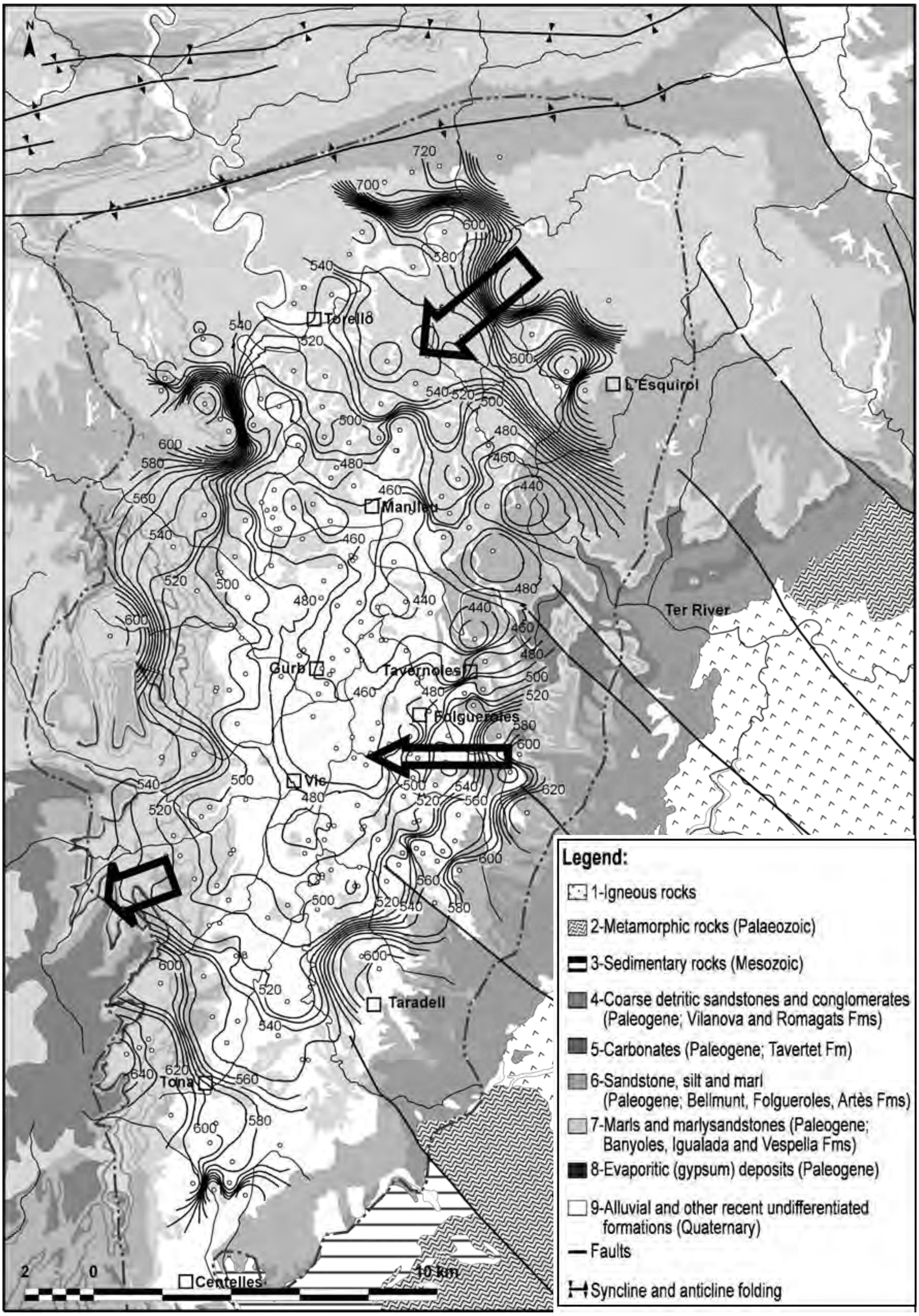


Figure 1.11 *– Potentiometric map of the Plana de Vic hydrogeological system (February 2005) showing the main flow direction and the different hydrogeological zones.Continuous black lines represent the isolines of potentiometry. Source: Menció et al., 2011b.*

The Plana de Vic area presents a groundwater flux that moves from the surrounding mountain areas to the center of the plain, especially form the eastern ranges to its central part. The Ter River has an important influence in the distribution of the groundwater level, as a discharge boundary, which is especially notable in the case of quaternary shallow aquifers.

The recharge area of the main aquifers in Plana de Vic is located in the mountain ranges situated in the north-eastern part of the study area, in Bellmunt and Cabrerès areas. At the east-southern part, the hills close to Folgueroles and Taradell are recharging the southern part of Plana de Vic. The influence of the mountain areas such as Montseny and Guilleries is limited due to the low hydraulic conductivity of the overlying Vilanova and Romagats Fms. The marls and marly-sandstones outcrops in the central part of Plana de Vic have a hydrogeological potential limited to their fracture network. Since they are not widely present at the surface, it is considered that superficial (alluvial) formations are recharging these layers. These superficial formations constitute unconfined aquifers, with groundwater downwards fluxes to deeper aquifers, especially when they are affected by groundwater withdrawal.

The Lluçanès plateau is hydrogeologically disconnected from the Plana de Vic system. The thick marl layers of Vespella Fm. impede a vertical flow relationship between the aquifer layers of the St. Martí Xic sandstones and the multilayered-aquifer system of Plana de Vic. In particular, the main aquifers of the Lluçanès plateau are found in the mentioned prograding sandstone levels of the St. Martí Xic deltaic formation, which mainly acts as a confined aquifer. Locally, small aquifer levels can also be found in the sandstones layers of the Artés Fm. However, its hydrogeological potential is limited to its lateral extent and the fact that the silt layers difficult an efficient recharge.

1.2.4 – Climatology

The Osona region has a sub-Mediterranean climate with hot summers and cool winters. According to an equally-weighted average from the weather stations at Gurb, Orís and Viladrau (Catalan Weather Service - SMC, 2012; Figure 1.12), the annual mean temperature is 12.6 ºC; and mean precipitation and potential evapotranspiration (using Thornthwaite equation) are around 715 and 706 mm/year, respectively. Spring and autumn are the rainiest seasons. In summer, potential evapotranspiration is usually twice as much precipitation.

The Plana de Vic area is subject to a natural phenomenon of thermal inversion, especially in the fall and in the winter time.

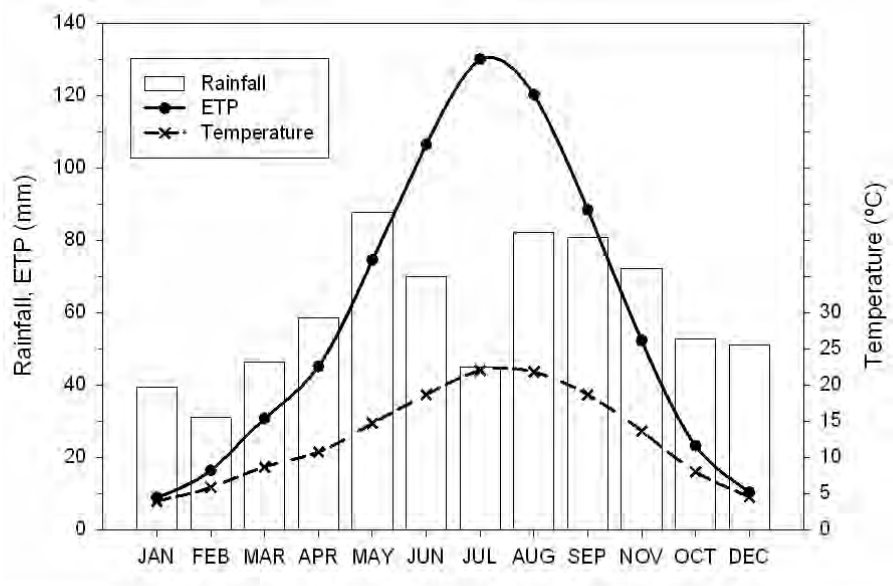


Figure 1.12 *– Climatogram for the Osona region (data from 1940 to 2000).*

1.2.5 – Agricultural and livestock activities

About 75% of the Osona region is covered by forests (91,296 ha), crops represent 20% of the total area (24,454 ha), only 3.7% corresponds to urban area (5,955 ha) and the rest (1.3%) are water bodies (Figure 1.13). The major land uses of Plana de Vic are agricultural and urban, meanwhile in the Lluçanès area are mainly agricultural and forested.

The most common crop in the Osona region is wheat, grown on 30% of the total cultivated land (7,219 ha), followed by barley (20%), corn (14%) and sorghum (5%), among other minor crops. About 98% of the total cultivated land (23,906 ha / 239.06 Km^2) are non-irrigated crops. In the case of spring wheat and barley, application of slurry as a fertilizer 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 fertilization is from mid-January to July and manure application from January to mid-June. Therefore, the fertilization regime of crops in a given watershed depends on the crop type, but as well on the convenience of the farmer.

Spain experienced a severe increase in the number of head of livestock during the last decades (Figure 1.14). Traditionally, farms were owned by families and had few hogs and enough land where to spread the manure produced. However, a new model of farming production became established in the 1970's, requiring a modernization of the farms and the introduction of new technologies. In Catalonia, as well as in the Osona region, this phenomenon was observed especially in the late 1980's and 1990's.

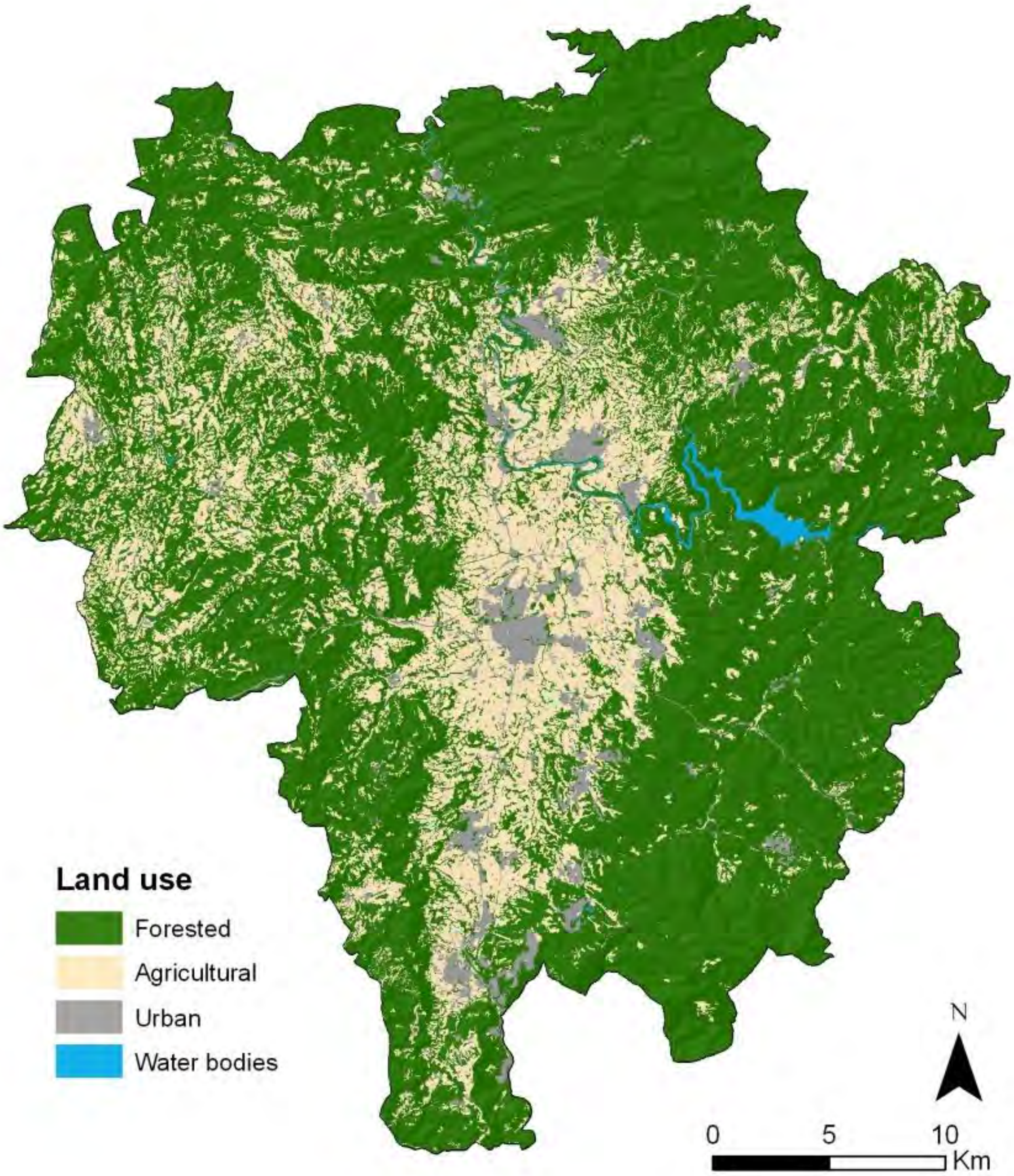


Figure 1.13 *– Land uses of the Osona region.*

The intensification of livestock activities was reflected in the farms and their productivity. A decrease in the number of farms with small capacity and an increase in animal feeding operations (AFOs) were observed. Consequently, more manure and slurry were produced and spread than the quantity recommended by law on the available crops in the surrounding areas. This resulted in nitrate leaching through the soil towards groundwater, causing water quality problems in the aquifers.

Osona is nowadays the region with the highest density of AFOs in Catalonia, with 2,261 farms in 2009 (including hogs, cattle, sheep, goats, horses, poultry and rabbits) and the third region with most hog animal feeding operations, after La Noguera and El Segrià regions.

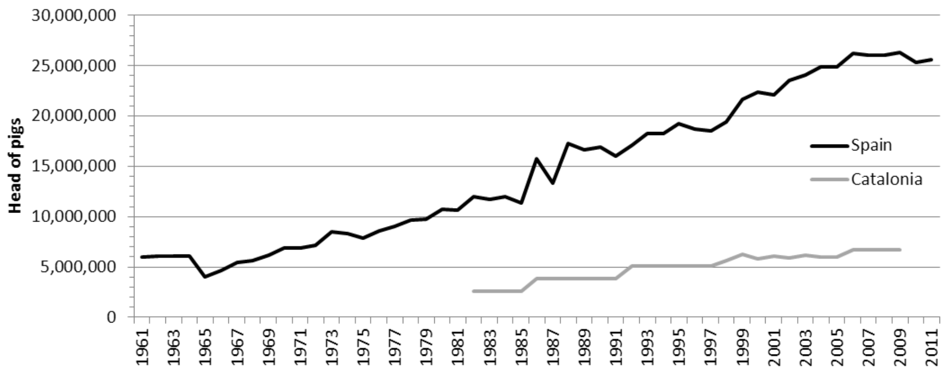


***Figure 1.14** – Evolution of head of pigs from 1961 to 2011 in Spain. Source: FAOSTAT, 2013; CADS, 2008; IDESCAT, 2013.*

In the Osona region, the number of head of pigs increased exponentially from 1986 to 1999. In 1999, there was a decrease in this number due to the swine fever outbreak (CADS, 2008). In 2006, another reduction was observed due to the economic crisis, which increased grain prices. At the same time, the number of hog AFOs decreased by 52% from 1999 to 2009. In 2009, there were 665 of them and held about 795,000 hogs (Figure 1.15). Osona also have about 68,500 head of cattle, including dairy and beef cattle (IDESCAT, 2013).

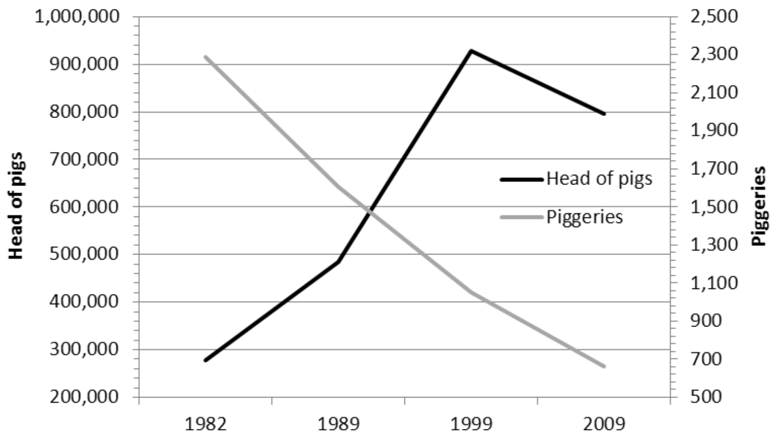


***Figure 1.15** – Evolution of head of pigs and AFOs in the Osona region from 1982 to 2009. Source: IDESCAT, 2013.*

Therefore, a big amount of organic fertilizers (manure and slurry) generated by livestock is produced every year (about 7,875 tons of N in 2010). The 90.6% of the manure (7,135 tons of N) is spread as fertilizer on the crops (24,454 ha), most of them situated in Plana de Vic, where most of the agricultural activity occurs. Therefore, taking into account the kg of nitrogen produced and not treated, and the hectares of crop land available in the Osona region, the nitrogen budget is 291.77 kg N/ha, while theoretically only 170 kg N/ha as manure should be applied following the Nitrate Directive. Consequently, crops have been over fertilized for several decades resulting in high nitrate concentrations in groundwater, commonly above 50 mg/L. Only 9.4% of the manure produced is treated in treatment plants. There are two manure treatment plants in the Osona region, located in two municipalities (Les Masies de Voltregà and Santa Maria de Corcó).

Due to the intensive livestock and agricultural activities, the Osona region was declared vulnerable to nitrate pollution from agricultural sources (European Nitrate Directive, 91/676/EEC). In 2009, a total of 38 out of 51 municipalities in Osona, which represents 70% of its area and the totality of its agricultural land, were designated Nitrate Vulnerable Zones by the Catalan Parliament (Decret 136/2009).

1.3 – LITERATURE REVIEW

Nitrate pollution in groundwater has been a major concern in the Osona region in the last decades. The intensive agricultural and livestock activity producing large amounts of manure and slurry, often applied in excess, resulted in high levels of nitrate in groundwater. Nitrate concentrations in groundwater are commonly above 50 mg/L, reaching up to 500 mg NO_3/L in some of the sampled wells.

Since 1989, water samples from natural springs were analyzed to get to know the occurrence of nitrate pollution of groundwater in the Osona region. In 1996, an environmental organization called “Grup de Defensa del Ter”, based in the Osona region, sampled some natural springs in Osona to analyze nitrate concentrations in water. Later on, they did an inventory of more than 1,000 springs and in 2000, they started an annual survey of some of these springs (GDT, 2005). In 1999, different wells and springs were sampled over to study the magnitude of nitrate pollution of groundwater in Osona. This study already stated that only 20% of the water samples had nitrate concentrations below the drinking threshold of 50 mg/L (Prat, 1999). Since then, several minor studies (unpublished), which analyze nitrate concentration in springs, have been carried out at different universities as undergraduate projects with only local value or interest.

At the same time, a local authority (Consell Comarcal d’Osona - CCO), also aware of nitrate pollution in groundwater, began a monitoring program in 2004 to survey the concentration of nitrates in about 100 natural springs. Two sampling campaigns per year (spring and fall) have been carried out since then. These reports remain unpublished, but are available to researchers under request.

The Catalan Water Agency (Agència Catalana de l'Aigua - ACA) has a monitoring network of several wells in the Osona region to assess the evolution of nitrate concentration and other water quality parameters in groundwater. Most of the wells are for drinking water supply.

In 2006, ACA, together with CCO and ASSAPORC (a farmer's private association) funded a project to study the hydrogeological dynamics of Plana de Vic and to perform a multi-isotopic analysis to characterize isotopically the hydrogeological system and to determine nitrogen sources (Mas-Pla et al., 2006). In 2008, a similar project, this time funded by ACA and CCO, was done in the Lluçanès region to characterize the hydrogeologic system in order to determine water resources, their pressures and to define protection areas for the main urban supply wells (Mas-Pla et al., 2008).

Both reports are unpublished; however, their main results were presented in peer-review journals. In Menció et al. (2011b), the spatial distribution and temporal variations of nitrate concentrations in wells were used to depict hydrogeological dynamics within the sedimentary aquifer system of Plana de Vic. This study pointed out that nitrate originates with infiltration from agricultural areas where large quantities of pig manure are used as fertilizer. In the case of deep wells (> 30 m) in this hydrogeological system, nitrate content results from two combined factors. On one hand, nitrate levels increase with significant recharge after a drought period. On the other hand, the movement of nitrate through fractured aquitards is induced by groundwater pumping, from upper layers with high nitrate concentration to deeper layers with low levels of nitrate. Moreover, the inadequate well construction such lack of casing result that water from all the productive layers is mixed.

Pioneer studies on nitrate dynamics and natural attenuation in the Osona region performing laboratory and field-scale experiments were conducted at Plana de Vic. For instance, Vitòria (2004) characterized the chemical and isotopic composition of organic (pig manure) and synthetic fertilizers, as nitrogen isotopic composition is a valuable tool to distinguish the source of nitrate contamination in water. In her Ph.D. dissertation, L. Vitòria used environmental isotopes to report the temporal occurrence of natural attenuation processes (denitrification) at 6 springs in a small area in Osona. Springs were chemically and isotopically characterized, which allowed identifying a continuous nitrate input throughout time and also showed that denitrification processes existed, first, due to the oxidation of organic matter contained in the manure and secondly, due to oxidation of pyrite.

Chemical and multi-isotopic approaches were applied to nitrate-contaminated water from wells and springs by Vitòria et al. (2008) in an area of 38 km^2 between the municipalities of

Manlleu and Torelló, in the Osona region. The coupled use of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ confirmed again the link between groundwater nitrate pollution and pig manure. Nitrate isotopic data also suggested that denitrification processes were taking place, mainly due to pyrite oxidation, in this large study area. The role of organic matter oxidation, however, could not be confirmed nor discarded.

Otero et al. (2009) used a multi-isotopic approach to assess the fate of groundwater nitrate, to characterize denitrification processes that control natural attenuation and to study their spatial and temporal variations in groundwater in Plana de Vic. This study linked the occurrence of denitrification processes in groundwater to pyrite oxidation, by coupling nitrate with sulfate isotopic data. Two main hydrogeological zones where natural attenuation was most effective were determined (north-east and south-west of the Osona region). An estimation of the isotopic enrichment factor was calculated using temporal variations of nitrate concentrations and the isotopic composition of dissolved nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$). Finally, an approximation of the degree of natural attenuation was performed in those samples presenting clear denitrification, and a median value of 30% of contaminant diminution was obtained.

Torrentó et al. (2011) used chemical, isotopic and microbiological techniques to test in laboratory experiments the extent to which the addition of pyrite to groundwater and sediments from a nitrate-contaminated aquifer could stimulate denitrification by indigenous bacteria. Results of this study show that the addition of pyrite enhanced nitrate removal and that denitrifying bacteria already existing in the aquifer were able to reduce nitrate using pyrite as the electron donor, with no need of inoculating autotrophic denitrifiying bacterium *Thiobacillus denitrificans* (bioaugmentation).

Laboratory and field-scale experiments (biodenitrification pilot-scale plant) were developed by Vidal-Gavilan et al. (2013) to test the viability of in situ heterotrophic denitrification in a fractured aquifer. Native microbiota was stimulated and nitrate reduction was effectively achieved of a carbon source (ethanol or glucose) as well as phosphorus source (disodium hydrogen phosphate). Sulfate isotopic characterization proved that autotrophic denitrification linked to sulfide oxidation could be occurring along with heterotrophic denitrification. Overall, results of this study suggested that biodenitrification could be applied as a remedial alternative at similar sites, even though efforts must be addressed to avoid side effects that could influence system performance and final groundwater quality.

1.4 – OBJECTIVES

The aim of this doctoral thesis is to study the occurrence of nitrate pollution in groundwater in the Osona region by monitoring natural springs and wells, focusing on its transport to the subsurface and assessing aquifer vulnerability.

The specific objectives to reach this main goal are to:

1) Characterize natural springs in the Osona region and to evaluate the major vulnerability factors that affect their nitrate concentration.

2) **I**nvestigate the hydrologic and hydrochemical responses of springs to rainfall regimes and land uses through time, with special emphasis on nitrate concentrations, in order to understand nitrate recharge rates to aquifers.

3) Identify spatial groundwater vulnerability through a regression model. This objective requires evaluating which variables significantly influence nitrate contamination in groundwater, as a prerequisite task to create vulnerability maps for the different aquifers in the region.

This research looks forward a comprehensive description of the hydrogeological processes that govern nitrate pollution in Osona, linking human pressures with the intrinsic properties of the aquifer to evaluate groundwater vulnerability, as a means to assess water resources management.

1.5 – STRUCTURE OF THE DOCTORAL THESIS

This doctoral thesis is divided into six sections. First of all, this introduction describes the frame in which this research lays and includes a geological description of the Osona region where the field work is conducted, some literature review, and the objectives of the dissertation. Next, results are presented in three chapters, each of them with its own introduction, methodology, results and discussion, and conclusions. It follows a general discussion considering all the topics that have been tackled in this dissertation. A conclusion chapter and the reference list end this volume.

Following, there is a summary of each chapter:

CHAPTER 1 – General introduction

The introduction includes a general description of the state of the water resources, focusing on groundwater, as well as an overview of the nitrate problem from a world-wide perspective to a local scale. Furthermore, the study area where the field work was conducted is introduced. In this section, the objectives of the PhD dissertation are also defined.

CHAPTER 2 - Analysis of vulnerability factors that control nitrate occurrence in natural springs (Osona, NE Spain)

In this chapter, the occurrence of nitrate in natural springs is used 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 twice annually 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 some 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 nitrate pollution in springs.

The results of the analysis identify a background 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 are 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 uses, and particularly fertilization practices, are major factors in groundwater vulnerability.

CHAPTER 3 - Temporal analysis of spring water data to assess nitrate inputs to groundwater in an agricultural area (Osona, NE Spain)

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 behaviors, nitrate content shows uniform values in most of the springs with only a minor influence from external factors such as rainfall events, fertilization regimes and geological traits. Such evenness of outflow might be attributed to a homogenization of the subsurface processes that determine nitrate infiltration after decades of intensive fertilization 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.

CHAPTER 4 - Regression model for aquifer vulnerability assessment of nitrate pollution in the Osona region (NE Spain)

A multiple linear regression (MLR) model was developed for the Osona region to determine aquifer vulnerability to nitrate pollution in groundwater. The MLR model was based on a data set of nitrate data from 57 private wells sampled in 2010. Up to 70 explanatory variables were screened to statistically identify the key parameters that determine nitrate concentration in groundwater in the study area. Finally, five variables were selected for the regression model, which are the following: 1) nitrogen loading as manure; 2) aquifer type; 3) percent of well-drained and deep soils; 4) percent of irrigated crops; and 5) an indicator of the presence of denitrification processes, which together represent the input of nitrogen, transport and attenuation of nitrate in groundwater.

The model features three innovations: net nitrogen input was determined throughout the region using a simple mass balance approach and a newly available GIS tool; the model addresses vertical aquifer heterogeneity; and detailed aquifer chemistry at well locations was incorporated into the spatial model by reducing data to composite variables for subsequent interpolation by kriging. All variables were significant in the MLR model (p-values<0.10) and explained 75% of the variation in groundwater nitrate concentrations. A plot of observed vs. predicted nitrate for 25 validation wells yielded a significant (p-value<0.001) and a positive correlation. Vulnerability maps for unconfined, leaky and confined aquifers were developed according to the calibrated regression model.

CHAPTER 5 – General discussion

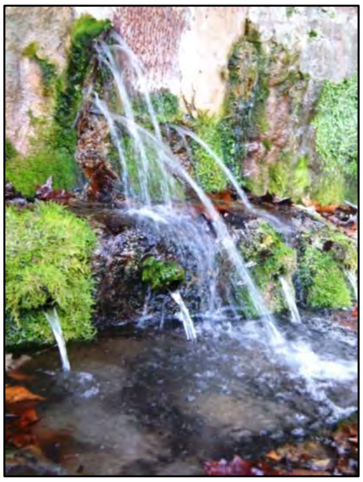
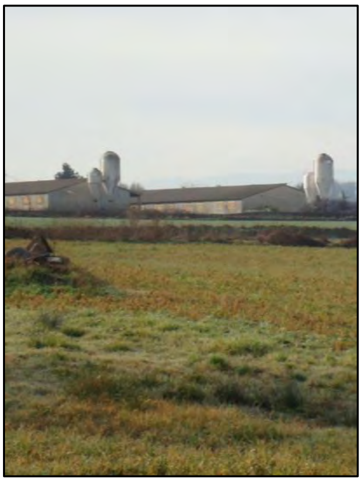
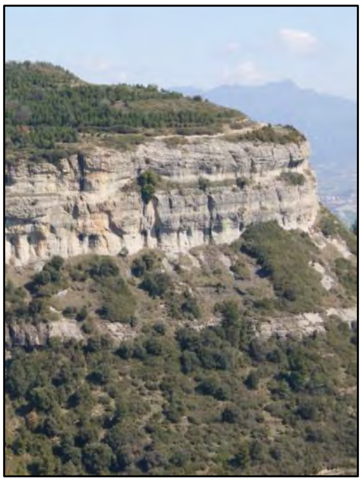
A general discussion is presented in this section linking all the outcomes of this dissertation with the aim to evaluate their contribution to the knowledge of the Osona hydrogeological system and its groundwater pollution, as well as to explain how they contribute to the achievement of the stated objectives.

CHAPTER 6 – General conclusions

The main conclusions of this research, extracted from the main findings of each chapter and including a conceptual model for nitrate occurrence in the Osona hydrogeological system, and potential management strategies are finally presented.

CHAPTER 2

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

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2.1 – 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 help 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 (Leibungut, 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 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), Rodwen 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 (Figure 2.1). It has an area of 1,260 km^2 and a total population of about 150,000 inhabitants. This is an intensive livestock production area, with 665 hog animal feeding operations in 2009, and more than 800,000 head of livestock. Manure generated by livestock production is spread as organic fertilizer on the 244.54 km^2 of the row crops (20% of the study area), most of them situated in 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

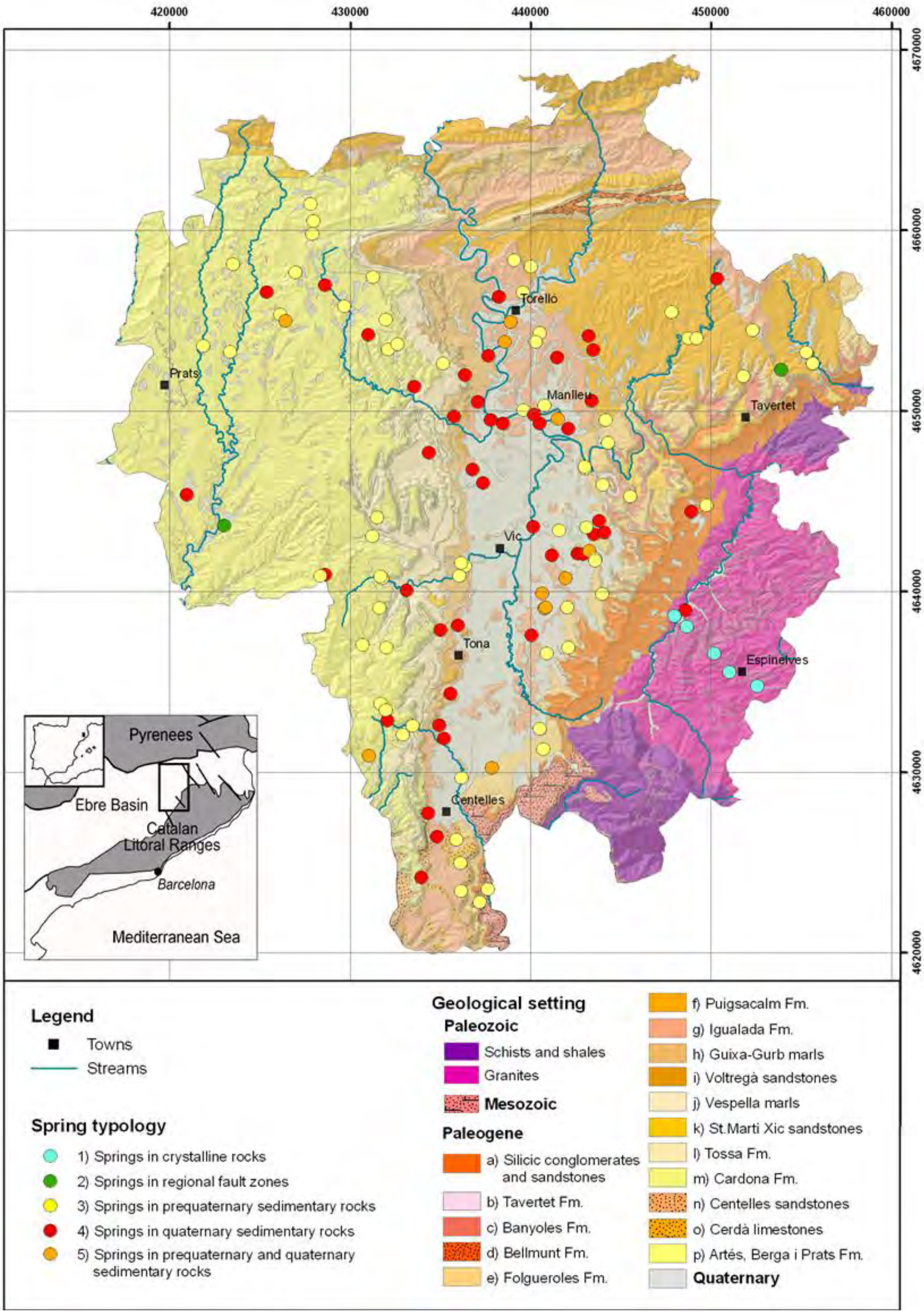

***Figure 2.1** – Map of the geographical and geological setting of springs and the study area.*

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 5-10º 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 (Figure 2.1).

Hydrochemical characteristics of these aquifers were described by Menció et al. (2011) obtaining three groundwater types in 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 et al. (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 are 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 period, 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.

2.2 – 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 Figure 2.2 and Table 2.1, 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 Figure 2.2 and/or Table 2.1), 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 changes within the same deposit; 4a) or depositional (i.e., associated with the deposit geometry and its geological boundaries; 4b) control over spring occurrence, and the type of deposit (alluvial, colluvial, eluvial, or mass-wasting) the spring is associated with.

Spring typology			Code	Land use		
				Agricultural	Forested	Urban
1. Springs in crystalline rocks			1	0	5	0
2. Springs in regional faults			2	0	2	0
3. Springs in pre-quaternary sediments	a) In karstic carbonate rocks		3a	1	1	0
	b) In marls and sandstones	1) With fractures	3b1	6	3	3
		2) Permeability changes	3b2	7	10	3
		3) Without distinction	3b	16	13	4
4. Springs in quaternary sediments	a) With sedimentary control	a/c) In alluvial or colluvial sediments	4a-a/c	2	0	1
		gl) In glacis	4a-gl	1	0	0
	b) With depositional control	1a/c) In alluvial or colluvial sediments	4b1-a/c	17	2	0
		1gl) In glacis	4b1-gl	2	0	0
		1g) In landslides	4b1-ls	0	5	0
		2e) In eluvial sediments	4b2-e	9	0	0
		1c/2e) In colluvial or eluvial sediments	4b1-c/2-e	4	1	0
5. Springs in pre-quaternary + quaternary sediments			3b1+4b	5	0	0
			3b2+4b	0	0	1
			3b+4b	5	0	0

***Table 2.1** – Number of springs according to their geological setting and land use in their recharge area.*

Some springs may originate from a complex geological setting that involves two types of the above-mentioned groups. Such diversity has been taken into account and those spring groups named as the sum of both indexes (e.g.: 3b1+4b, 3b2+4b or 3b+4b, Table 2.1).

These geological details can be expected to control the flow regime (its direction and magnitude) in the uppermost layers of the subsoil, and consequently, are an intrinsic vulnerability factor for determining nitrate concentration in the spring discharge. If the statistical significance of the geology is revealed, it will help to improve the plotting of vulnerability maps for nitrate pollution.

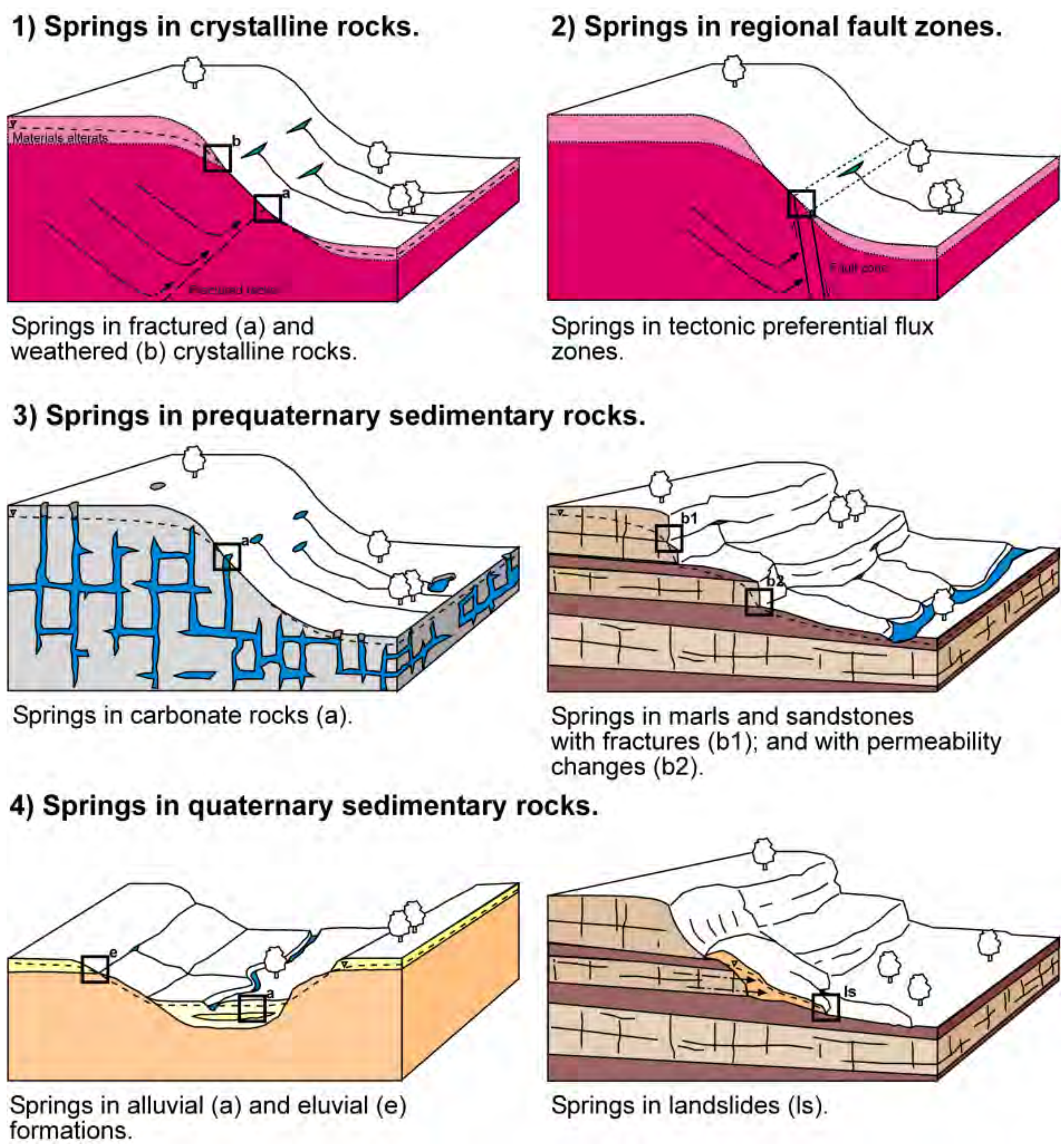

***Figure 2.2** – Spring typology according to geological setting.*

2.3 – METHODOLOGY

2.3.1 – Sampling, chemical analysis and spring classification

The data used in this study proceed from ten different sampling surveys carried out by the local authority. Although up to 400 water samples were collected in different campaigns, the numbers used in this analysis are as follows: October-November 2004 (C1, n=34), April-May 2005 (C2, n=82), October 2005 (C3, n=83), April-May 2006 (C4, n=81), October-November 2006 (C5, n=86), April-May 2007 (C6, n=17), October 2007 (C7, n=78), April-May 2008 (C8, n=78), October-November 2008 (C9, n=85), April 2010 (C10, n=109).

Samples were transported and stored at 4ºC. Nitrate was analyzed in the laboratory with a UV-visible spectrophotometer (lambda 2) from Perkin Elmer. This method presents an mean error of 1%, and a detection limit of 0.1 mg NO_3^- /L. Electrical conductivity (EC) and pH were determined in the lab the same day of sampling a few hours after collection with Crison CM35 and pH25 meters, respectively.

Springs were classified according to their geological setting (as described), and then according to land use (agricultural, urbanized, or forested) in their recharge area (Table 2.1).

2.3.2 – Hydrochemical background determination

Background values for nitrate were determined to establish the threshold above which concentrations could be attributed to anthropogenically-induced processes only. One of the assumptions required for background analysis is proof of relative homogeneity, which enables results to be compared with the entire hydrogeological system (Matschullat et al., 2000). In order to allow this assumption to be made, springs located in Hercynian materials were ruled out, and the background analysis only focused on springs situated in sedimentary materials (groups 3 and 4, as shown in Table 2.1 and Figure 2.2).

Relative cumulative frequency curves were selected to determine nitrate background in the study area. This technique does not require any assumptions about a specific distribution function. It divides water samples into two or more populations separated by inflection points on cumulative probability graphs (Matschullat et al., 2000; Panno et al., 2006). Maximum curvature of the lines reveals inflection points or threshold values between populations, and the first bend of the slope in the curve is defined as the upper limit of any background data set (Bauer and Bor, 1993 and 1995; Bauer et al., 1992).

In accordance with Panno et al. (2006), NO_3^--N concentrations in the springs were log-transformed prior to generating cumulative probability plots. Two different plots were drawn: a) one considering all the springs in sedimentary materials; and b) one considering only springs in sedimentary materials in forested land, the most pristine area in the region.

2.3.3 – Statistical analysis

Logistic regression was applied to predict whether different geological features of the springs' locations, as well as their water characteristics, act as true, distinct vulnerability factors (independent variables) that significantly control nitrate concentrations. The aim of this part of the project was not to obtain a model which describes nitrate occurrence in the Osona region, but to test the importance of different factors on nitrate pollution. For this reason, all the variables, significant or not, were maintained through this analysis. Nitrate values were used as a dependent variable and converted to a binary response of 0 if the nitrate concentration was under the background threshold of 8 mg NO_3^-/L and 1 if it was over this value. Independent variables included the geological settings of springs, main land use in their recharge area, the field campaign in which they were analyzed, and the pH and electrical conductivity of their water.

Categorical variables such as the geological setting, land use and the campaign were converted to dummy variables. A dummy variable is a numerical variable with only two values, 0 and 1, used in regression analysis to represent subgroups of the sample variables. Dummy variables enable to use a single regression equation to represent multiple groups. Therefore, variables were transformed into a metric variable by assigning a 1 or a 0 to a subject, depending on whether it possesses a particular characteristic (Hair et al., 1998). For instance, a value of 1 for springs located in forested areas and a value of 0 was given to springs located in agricultural and urban areas.

In a generalized logistic regression analysis with dummy coding, a particular category of responses is chosen as the reference group and all of the other groups are compared to the reference group, thus converting these categories in independent variables. With dummy coding, the group with all dummy variables equal to zero becomes the reference group. Two different associations of springs were used to test the geological setting. The first grouping considered nine different types of springs: 3a (n=2), 3b (n=33), 3b1 (n=12), 3b2 (n=20), 4a (n=4), 4b (n=40), 3b+4b (n=5), 3b1+4b (n=5), and 3b2+4b (n=1). In the second broader grouping, there are only three categories: springs in pre-quaternary formations (3, n=44), springs in quaternary deposits (4, n=67), and springs associated with the both kinds of geological setting (3+4, n=11). All the spring categories in both classifications are mutually exclusive, even the ones that appear to be combinations of other categories. For instance, group 3b+4b includes springs that drain quaternary sediments (4b) and pre-quaternary rocks (3b) as we could not distinguish whether their origin was caused due to permeability variations or fractures in the pre-quaternary rocks.

These two levels of classification were considered to analyze the statistical significance of the classification of the springs according to their hydrogeological setting. In the most detailed classification, some of the spring groups could not be considered as part of the statistical analysis because of the low number of samples, but most of the main groups, such as 3b, 3b1, 3b2, 4a and 4b, were always compared. As a result, the first model comprised 19 independent variables, and the second one, 13 independent variables.

The large size of the spring database enabled us to simultaneously analyze all the factors because, as a rule of thumb, the number of independent variables that was 19 or 13 depending on the spring classification, was smaller than m/10, where m is the number of data sets or the number of observations (m=733; Harrel et al., 1996; Liu et al., 2005). An independent variable is considered significant if it has a p-value (i.e., the value for a Wald chi-square statistic with respect to a chi-square distribution) less than 0.05 (95% confidence), and the upper and lower 95% confidence interval does not straddle 1. Only 554 of the 733 observations were used in the LR model, which requires all variables for every sample. This data discrepancy was caused by the lack of EC and pH data for two campaigns (C8, in April-May 2008; and C9, October-November, 2008), and the result of m/10 is still higher than 19 and 13.

Additionally, an analysis of variance (ANOVA) was conducted to test not only if nitrate variance in contaminated springs could be accounted for by land use, but also if the geological setting could account for part of the nitrate variance independently of land use. Before conducting the ANOVA, the Levene test was conducted to test homogeneity of variances.In this examination springs with concentrations under the background value were ruled out, and a square root of NO_3^- transformation was used to obtain a normal distribution of the data set for each campaign. Using this transformation all the campaigns obtained p-values over 0.05 in both the Kolmogorov-Smirnov test and the Shapiro-Wilk test, which was used for campaigns with less than 30 pieces of data. A new independent variable was created combining two levels of classification of springs according to their geological setting and land use in their recharge areas: agricultural, urban or forestry.

2.4 – RESULTS AND DISCUSSION

2.4.1 – Nitrate distribution and temporal evolution

To analyze nitrate distribution in Osona springs, 131 of 400 sampling points were selected according to their geological setting representativeness, sampling frequency, and nitrate concentration range (Figure 2.1). Throughout the ten campaigns, nitrate ranged from concentrations under the detection limit (<0.1 mg NO_3^-/L) to values up to 438 mg/L. As many as 53% of the springs presented mean nitrate concentrations higher than 50 mg/L, which is the nitrate concentration threshold for drinking water. According to Table 2.2, the highest concentrations were always associated with springs with agricultural activity in their recharge area, with a mean value of 108.2±3.7 mg NO_3^-/L; while the lowest concentrations corresponded to springs in forested areas, with a mean value of 14.5±1.8 mg NO_3^-/L. Springs in urban areas presented mean concentrations of 76.0±6.0 mg NO_3^-/L.

Variable	Subcategory	Mean	SE	SD	Num.	%
Land use	Agricultural	108.2	3.7	81.6	346/473	73.15
	Forested areas	14.5	1.8	22.1	12/258	4.65
	Urban areas	76	6	53.6	59/96	61.45
Geological setting	G1: crystalline rocks	4.8	0.1	3.7	0/35	0
	G2: regional faults	3.5	0.8	2.8	0/12	0
	G3: prequaternary sediments	55.6	3.2	65.66	154/407	37.83
	G4: quaternary sediments	105.0	5.6	91.6	94/269	34.94
	G5: G3+G4	98.7	7.1	62.8	16/79	20.25

Table 2.2 *– Nitrate distribution according to land use and geological setting. Legend: Mean, mean nitrate concentration in mg NO_3^-/L; SE, standard error; SD, standard deviation; Num., number of analyses in springs with nitrate concentrations higher than 50 mg NO_3^-/L with respect to the total number of samples in this category; %, percentage of samples in this category with concentrations higher than 50 mg NO_3^-/L.*

Springs with the lowest concentrations were those located in crystalline rocks or along regional faults, where nitrate concentrations were always under 50 mg NO_3^-/L. The highest concentrations were detected in springs in sedimentary materials: in pre-quaternary sediments (group 3), with mean values of 55.6±3.2 mg NO_3^-/L; in quaternary sediments (group 4), with a mean value of 105.0±5.6 mg NO_3^-/L; and in pre-quaternary and quaternary sediments (group 5), with a mean value of 98.7±7.1 mg NO_3^-/L (Table 2.2).

Figure 2.3 uses box plots to represent nitrate evolution during the period under study, and the results of the Wilcoxon test for paired scores non-normally distributed, used to determine whether these changes are statistical significant, are represented with the grey line. Average monthly precipitation (P) and potential evapotranspiration (PET; using Thornthwaite equation) are also represented. A decreasing trend in nitrate concentration was observed, starting in October 2004 and lasting until October 2005. A certain amount of nitrate increase was registered in April 2006, followed by another decrease in the next survey that was maintained until April 2008, which coincided with a general drought (2006 - 2008) only interrupted by specific rainfall events. Finally, an increase in the last two surveys was observed following a rainy fall and winter. Thus, there is not a general trend of gradual increase or decrease in nitrate concentrations in springs throughout the period under study, although a relationship can be established with the main recharge periods.

Nitrate occurrence trends in springs are related to the seasonal and annual variation of rainfall, as well as the response of small-scale hydrogeological systems to agricultural activities, in particular the application of pig manure as a fertilizer. During the period under study, the wettest year was 2008 with a mean annual rainfall of 905.2 L/m^2 (from May to December), while 2006 and 2007 were the driest ones with 558 and 486.5 L/m^2, respectively. During low rainfall periods, mean nitrate concentrations decreased in the first subsequent sampling surveys; when medium rainfall events took place, nitrate concentration was maintained; and finally, when high precipitation events occurred, mean nitrate concentration tended to increase, as observed in the last two surveys.

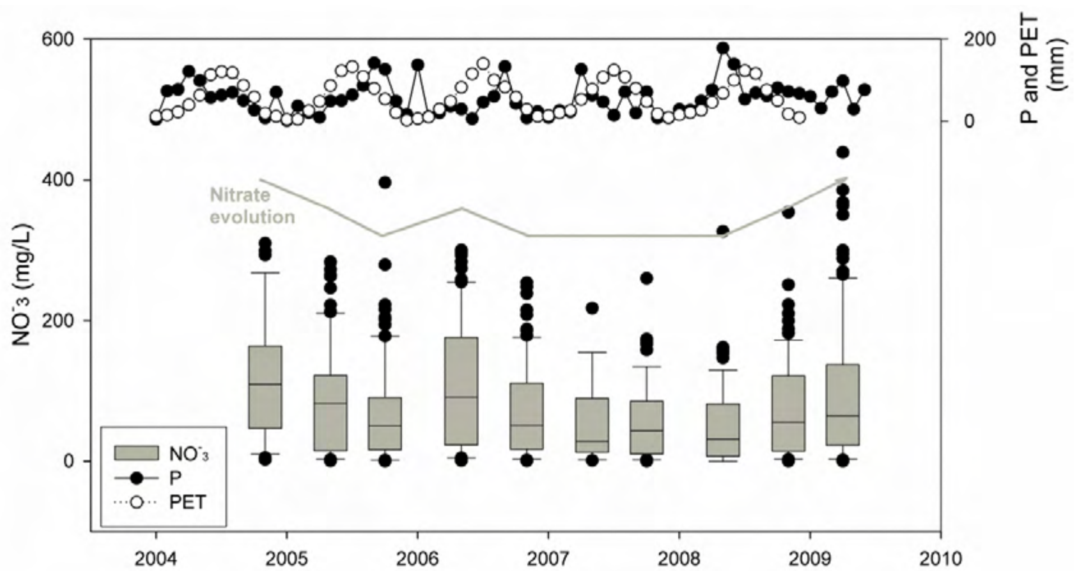

Figure 2.3 *– Nitrate evolution (in mg/L) represented by box plots, precipitations and potential evapotranspiration (in mm; using Thornthwaite), during the study period. The grey line represents statistically significant changes on nitrate concentration between sampling periods, according to the Wilcoxon test for paired scores non-normally distributed; that is nitrate evolution during the study period.*

Such a broad correlation points to the relevance of the leaching effect of rainfall infiltration on soils. Intense rainfall events produce an effective infiltration of nitrate-rich water towards the subsurface, a consequent aquifer recharge, and the response of natural springs through the subsoil's high hydraulic conductivity layers and fractures that feed them. During dry periods, springs are characterized by a lack of percolation, as nitrate is stored in the soil pore water, and the discharge is fed by preferential flow paths that do not efficiently remove stored nitrate in the soil and in the uppermost unsaturated layers of the aquifer. Subsequent intense rainfall events will produce the percolation of all soil pore water as shown by the nitrate increase. In terms of general behavior, the leaching process, which contributes to an increase in nitrate concentration in spring water, indicates that any expected dilution of nitrate levels by infiltrating rainfall will not be significant, if it actually takes place.

This observed behavior is in contrast to the response of large karst springs, where in some cases most of the nitrate load exits the basin through the springs as base flow, and the remaining load is discharged as a result of fast recharge associated with precipitation storm pulses (Peterson et al., 2002). Burg and Heaton (1998) and Katz et al. (2004) observed that highest nitrate concentrations occur during base flow periods of matrix drainage, while lower concentrations more related to fissure flow were observed during high rainfall/recharge conditions, when the amount of mixing with surface water was higher.

2.4.2 – Background analysis

Cumulative probability graphs of the NO_3^--N data for springs in sedimentary formations are shown in Figure 2.4. Two clear inflection points, or thresholds, were identified at the lowest concentrations of the graphs, at ≈0.4 and 6.8 mg NO_3^-/L in the graph for all the evaluated springs, and ≈0.4 and 7.8-15.71 mg NO_3^-/L for springs in sedimentary formations with forested land in the recharge area. The first inflection point is influenced by the volume of data under the detection limit (n=44 of the total samples considered). The second can be considered as the real threshold value for nitrate background concentrations in this area. Although this technique is recommended for use in springs in pristine areas (Matschullat et al., 2000; Panno, 2006), we have applied it for all the springs, including those which drain agricultural and urbanized areas. As the sampling effort is designed to take into account all the different situations in the Osona region, the threshold value for nitrate background concentrations will appear as the lowest nitrate concentration inflection point, while other inflection points at higher nitrate values should be indicators of distinct quality problems for higher concentration ranks. Thus, as pointed out previously, cumulative probability graphs show similar threshold values for all springs rather than just for springs located in pristine areas, i.e., those with a forested recharge area, which is consistent with the available data.

Hence, samples with NO_3^- concentrations higher than approximately 8 mg/L are defined as representing anthropogenic contamination.

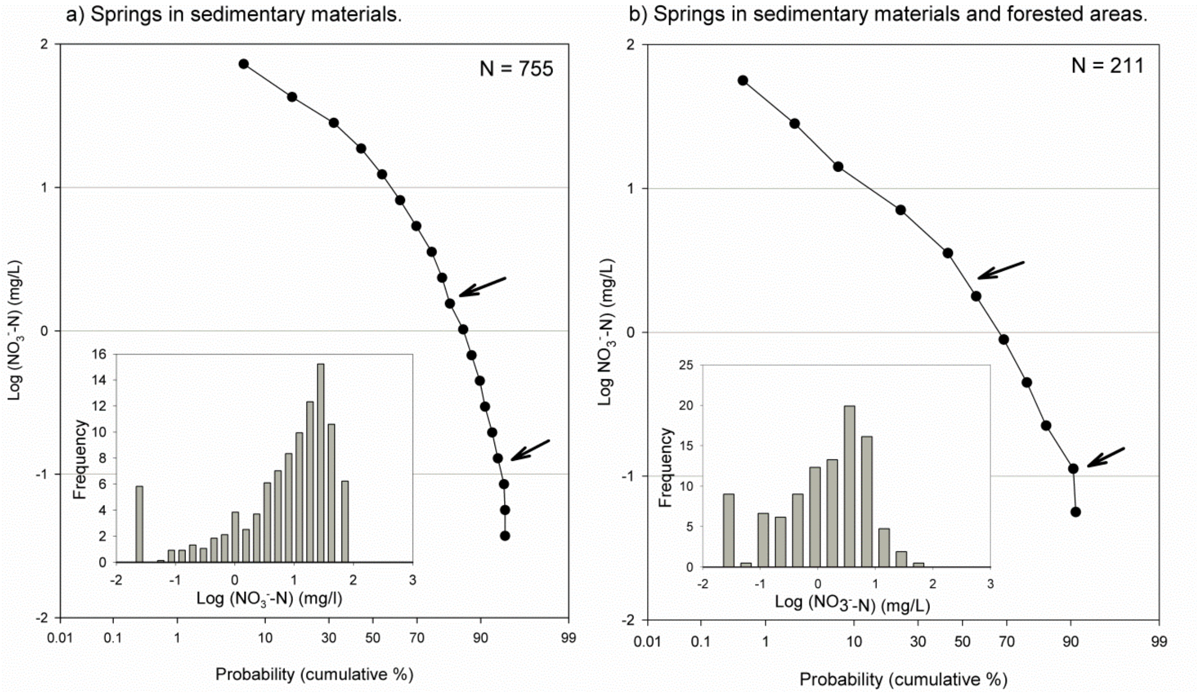

Figure 2.4 – *Cumulative plot distribution of NO_3^--N in the study area, and determination of the background threshold.*

2.4.3 – Statistical analysis of major factors affecting nitrate in springs

Logistic regression (LR) was conducted to analyze whether the potential risk factors in NO_3^- concentration, identified in the study area, are key factors to explain nitrate pollution. This analysis was performed including all factors at the same time. The results of this analysis are shown in Table 2.3 and 2.4. Two standards, where 1) *p*-value is less than 0.05% (95% confidence), and 2) the upper and lower 95% confidence intervals do not straddle 1, were applied to estimate the significance of each vulnerability factor.

In this test, four different independent variables showed significant influence on NO_3^- pollution (land use, geological setting, water EC, and water pH) and the only variable that did not show any influence on nitrate pollution was the sampling campaign.

The estimated coefficients indicate the amount of change expected in the log odds when there is a one unit change in the predictor variable with all of the other variables in the model held constant. The sign of the log-odds ratio indicates the direction of its relationship, whether there is a positive relationship between the explanatory variable and the likelihood of a success, or a negative relationship. The odds ratio (OR), which is the exponential of the log-odds ratio, gives an intuitive sense of how much things are changing. As mentioned, for the log-odds ratios, a negative value indicates a negative relationship, but all odds-ratios are positive values. The distinction regarding a positive or negative relationship in the odds ratios is given by which side of 1 they fall on. The value of 1 indicates no relationship, while less than 1 indicates a negative relationship, and greater than 1 indicates a positive relationship.

As regards quantitative variables, pH showed a negative coefficient, and also an odds ratio (OR) lower than 1, which indicates that a decrease in pH can result in an increase in the possibility of spring waters with higher NO_3^- concentrations. Although in this area nitrate attenuation by sulfide oxidation was reported, nitrate leakage to the aquifers was the main process that controlled high nitrate concentrations observed by Otero et al. (2009) and Menció et al. (2010).

Thus, this negative relation between NO_3^- and pH is consistent with nitrification of NO_2^- and NH_4^+ at the soil and the uppermost layers of the subsurface drained by springs, which produces an increase in H^+ in the water solution (Stumm and Morgan, 1981). However, a positive coefficient for EC indicates an increased possibility of higher NO_3^- concentrations in spring waters, which is consistent with the increase observed in chloride, sulfate and selected cations, usually calcium, when organic fertilizers are used.

As for dummy variables, the land use term compared agriculture and urban uses with forested areas. The OR obtained for these two categories of land use showed that the possibilities of having higher NO_3^- concentrations in agricultural and urban areas are 39.8 and 10.8 times greater than in forested areas.

In the first classification of springs according to their geological setting (3a, 3b, 3b1, 2b2, 4a, 4b, 3b+4b, 3b1+4b and 3b2+4b), the reference group for the dummy transformation was 3b+4b. Some groups, such as 4a and 3b2+4b, presented high OR and p-values, because they did not have a spring in a forested area. Most of the groups showed no significance with respect to the 3b+4b group, but 3b was found to be statistically different, allowing the geological setting to be classified as a significant variable for nitrate pollution (Table 2.3).

Variable	Coeff.	SE	p-value	OR	Low 95%	High 95%
Land-use			0.000			
Agricultural	3.685	0.464	0.000	39.842	16.055	98.869
Urban	2.387	0.557	0.000	10.880	3.653	32.405
Spring2			0.000			
3a	0.257	1.584	0.871	1.293	0.058	28.822
3b	2.630	1.000	0.009	13.871	1.954	98.448
3b1	1.149	1.028	0.264	3.155	0.421	23.655
3b2	0.137	0.955	0.886	1.147	0.177	7.452
4a	18.133	10369.473	0.999	7.5×10^{7}	0.000	.
4b	1.229	0.967	0.204	3.418	0.513	22.765
3b1+4b	0.741	1.322	0.575	2.097	0.157	27.965
3b2+4b	19.777	22852.996	0.999	3.88×10^{8}	0.000	.
Campaign			0.229			
C1	-0.144	0.878	0.869	0.866	0.155	4.842
C2	-0.657	0.560	0.241	0.518	0.173	1.554
C3	-0.574	0.564	0.309	0.563	0.187	1.701
C4	-0.019	0.556	0.973	0.982	0.330	2.918
C5	0.018	0.566	0.975	1.018	0.336	3.086
C6	-0.960	0.868	0.269	0.383	0.070	2.100
C7	-1.331	0.540	0.014	0.264	0.092	0.761
EC	0.002	0.000	0.000	1.002	1.001	1.003
pH	-0.383	0.146	0.009	0.682	0.512	0.908

Table 2.3 *– Results of logistic regression of the first classification of springs. Legend: Coeff, coefficient of logistic regression; SE, standard error; p-value, Wald chi-square statistic with respect to chi-square distribution; OR, odds ratio; Low95% and High95%, lower and upper confidence intervals. Reference groups in dummy variables: forested areas in land use; 3b + 4b in spring typology; C10 in campaigns.*

Variable	Coeff.	SE	p-value	OR	Low 95%	High 95%
Land-use			0.000			
Agricultural	3.236	0.418	0.000	25.443	11.217	57.708
Urban	1.903	0.497	0.000	6.705	2.533	17.749
Spring1			0.712			
3. Pre-quaternary	0.592	0.720	0.410	1.808	0.441	7.411
4. Quaternary	0.530	0.748	0.478	1.699	0.392	7.360
Campaign			0.422			
C1	-0168	0.790	0.832	0.846	0.180	3.979
C2	-0.556	0.505	0.271	0.574	0.213	1.543
C3	-0.514	0.517	0.320	0.598	0.217	1.648
C4	0.023	0.508	0.964	1.023	0.378	2.768
C5	0.119	0.523	0.820	1.126	0.404	3.137
C6	-0.077	0.851	0.928	0.926	0.175	4.904
C7	-1.028	0.500	0.040	0.358	0.134	0.953
EC	0.002	0.000	0.000	1.002	1.001	1.003
pH	-0.296	0.116	0.011	0.743	0.592	0.934

Table 2.4 *– Results of logistic regression of the second classification of springs. Legend: Coeff, coefficient of logistic regression; SE, standard error; p-value, Wald chi-square statistic with respect to chi-square distribution; OR, odds ratio; Low95% and High95%, lower and upper confidence intervals. Reference groups in dummy variables: forested areas in land-use; pre-quaternary and quaternary materials in spring typology; C10 in campaigns.*

Although the geological setting of the spring does indeed seem to be a factor which influences nitrate pollution, this effect can also be controlled by another variable, such as land use. For this reason, an ANOVA analysis that considered contaminated springs (those with NO_3^- concentrations above 8 mg/L) against geological setting and land use, while also comparing land use and geological setting together, as a new categorical variable, was carried out (Spring1+Land Use, and Spring2+Land Use, Table 2.5).

In the ANOVA analysis resulting from comparing contaminated springs and land use, significant differences are found between agricultural and forested areas. However, these differences are not observed between urban and agricultural uses, or between urban and forested areas (Figure 2.5, Table 2.5). When only the hydrogeological setting is considered, differences between groups of springs, such as 3b2 and 4b (in campaigns 4, 7, 9 and 10) and 3b and 4b (in campaign 10), are observed (Figure 2.5). These groups have clearly different land uses: 35-48% of the springs in groups 3b and 3b2 are located in agricultural areas, while 80% of the springs in 4b have this land use in their recharge areas (Table 2.1).

In the simultaneous ANOVA analysis of geological setting and land use, differences are observed between groups of springs with distinct land uses in their recharge areas.

Campaign	**Land use**		**Spring1**		**Spring2**		**Spring1 + land use**		**Spring2 + land use**	
	F	**p-value**	**F**	**p-value**	**F**	**p-value**	**F**	**p-value**	**F**	**p-value**
C1	16.684	<u>0.000</u>	1.708	0.182	3.488	<u>0.043</u>	4.081	<u>0.005</u>	6.222	<u>0.001</u>
C2	20.844	<u>0.000</u>	1.893	0.123	4.102	<u>0.021</u>	3.656	<u>0.001</u>	8.632	<u>0.000</u>
C3	9.865	<u>0.000</u>	1.420	0.239	2.398	0.098	2.629	<u>0.008</u>	4.135	<u>0.003</u>
C4	12.870	<u>0.000</u>	3.065	<u>0.023</u>	5.904	<u>0.004</u>	2.918	<u>0.003</u>	6.433	<u>0.000</u>
C5	15.004	<u>0.000</u>	1.382	0.251	3.209	<u>0.046</u>	2.893	<u>0.003</u>	6.570	<u>0.000</u>
C6	6.044	<u>0.014</u>	3.313	0.069	6.427	<u>0.024</u>	3.390	<u>0.047</u>	6.241	<u>0.008</u>
C7	14.506	<u>0.000</u>	2.627	<u>0.044</u>	4.621	<u>0.013</u>	3.092	<u>0.002</u>	6.602	<u>0.000</u>
C8	12.475	<u>0.000</u>	1.574	0.194	4.029	<u>0.022</u>	1.989	<u>0.043</u>	5.926	<u>0.000</u>
C9	9.905	<u>0.000</u>	3.606	<u>0.011</u>	8.728	<u>0.000</u>	2.200	<u>0.023</u>	9.026	<u>0.000</u>
C10	19.021	<u>0.000</u>	3.192	<u>0.017</u>	6.450	<u>0.002</u>	3.474	<u>0.000</u>	6.013	<u>0.000</u>

Table 2.5 – *ANOVA main results for each test conducted. F, is the coefficient obtained in the Fisher test; Spring1, first classification of springs; Spring2, second classification of springs; and underlined numbers are significant p-values.*

For instance, 3b in forested areas and 4b in agricultural areas, 3b in forested areas and 3b in agricultural areas, and 3b2 in urban areas and 3b in agricultural areas (Figure 2.5, Table 2.5). No differences were detected between groups of springs with the same land use in their recharge area. This means it is not possible to detect different behavior in springs on the basis of their geological setting.

Agricultural activities have a strong influence on the nitrate content observed in springs, regardless of their geological setting. Even if geological setting accounts for part of the nitrate pollution variance in springs, its significance is reduced because land use masks the potential relevance of geology (Table 2.5). This effect is more evident when the second geological setting classification is considered. In this case, all the variability accounted for by the geological setting is still better accounted for by land use. A Wald p-value higher than 0.05 is obtained in the simultaneous LR, meaning that this variable (geology) is not statistically significant in nitrate pollution in Osona springs (Table 2.4). In the ANOVA analysis, some differences can also be seen between pre-quaternary (group 3) and quaternary (group 4) springs. These are related to distinct land uses (Figure 2.6): while 51.3% of the springs located in pre-quaternary rocks have agricultural uses in their recharge area, only 34.6% are situated in forested areas and 14.1% in urban areas. For quaternary formation springs, 79.5% are affected by agricultural use, 18.2% by forestry, and only 2.3% by urban development.

Finally, there is a seasonal trend to spring nitrate content, but it does not determine the occurrence or absence of nitrate pollution. This shows that the hydrological response of these local, shallow, hydrogeological systems is more controlled by land use activities, namely crop fertilization with manure, than by rainfall distribution. Both pre-quaternary and quaternary formations react similarly to these governing variables.

2.5 – CONCLUSIONS

Most of the natural springs in the Osona region are affected by nitrate pollution and are mainly located in agricultural or urbanized areas.

An increase in nitrate evolution is mainly associated with heavy rainfall periods, while concentrations tend to decrease during long dry periods. Since these springs generally occur in the most superficial part of the aquifer, it can be stated that nitrate loadings to groundwater principally occur during heavy rainfall/recharge events.

The threshold value for nitrate background concentration has been determined by taking into account both sedimentary springs in pristine areas, and all the sedimentary springs. Because of the representativeness of the springs selected, the inflection points in both cumulative frequency plots are similar. Thus, in the Osona area the threshold value for nitrate background concentration has been set at 7-8 mg NO_3^-/L.

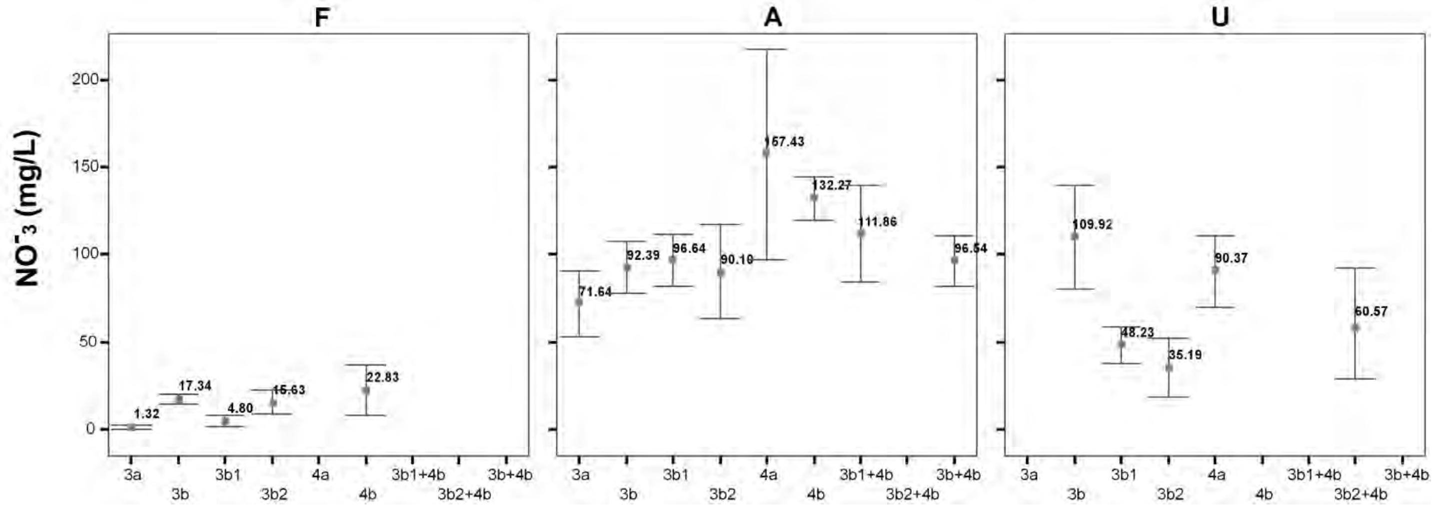

Figure 2.5 – *Error bar diagrams for nitrate concentration vs. land use and geological setting 1 (95% confidence). Mean values of nitrate concentrations are represented in each error bar. Legend: F, forest areas; A, agricultural; U, urban areas.*

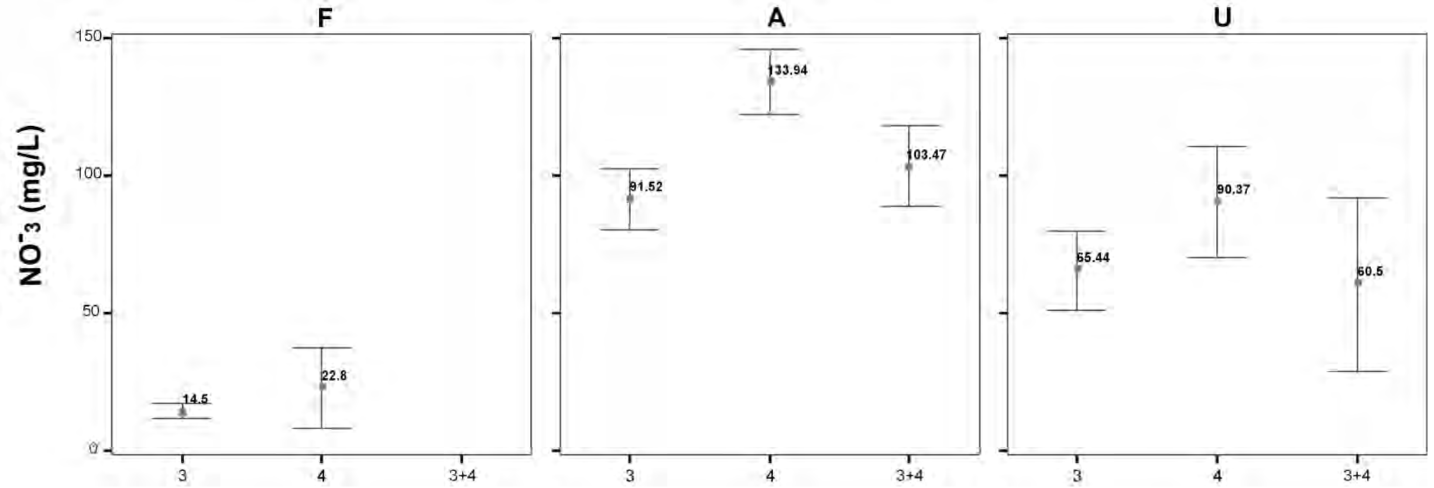

Figure 2.6 *– Error bar diagrams for nitrate concentration vs. land use and geological setting 2 (95% confidence). Mean values of nitrate concentrations are represented in each error bar. Legend: F, forest areas; A, agricultural; U, urban areas.*

Taking this value as the initial point, the results of the LR and the ANOVA analyses are as follows:

- An increase in EC or decrease in pH can be associated with increases in nitrate concentrations.
- Land use is a key factor in identifying the possibility of nitrate pollution in springs.
- In the Osona region, although the geological setting of a spring can account for part of the variance of nitrate pollution, the influence of land use masks its possible effect.

In conclusion, the data and their statistical analysis suggest that geological setting is not capable of buffering nitrate infiltration to groundwater. Consequently, nitrate-rich recharge will equally affect both local hydrogeological systems, concentrated in quaternary (mainly alluvial) formations, and regional aquifers, constituted by the fractured marl and sandstone formations outcropping in the hills in the Osona area, which form the basement of the quaternary aquifers.

CHAPTER 3

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

This is an edited version of the manuscript published in:
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3.1 – 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 considered nitrate to be one of the main contaminants that could impede the achievement of the objectives of Water Framework Directive 2000/60/EC. 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) 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. Moreover, they directly influence streams and other surface water bodies into which they discharge, including all dependent ecosystems. The monitoring of springs can thus reveal the vulnerability of an 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 characterized 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.

The determination of the spatial distribution and temporal variability of hydrochemical constituents (whether natural or anthropogenic) in groundwater is recognized 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). Long-term time series can be used to demonstrate the trend and temporal structure of a data set (Hipel and Mc Leod, 1994; Worrall and Burt, 1999) and therefore to investigate hydrological processes that occur in the subsurface (Rein et al., 2004; Wilcox et al., 2005).

The Osona region (Barcelona, NE Spain) is an area rich in natural springs due to its geological and geomorphological characteristics (Figure 3.1). 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).

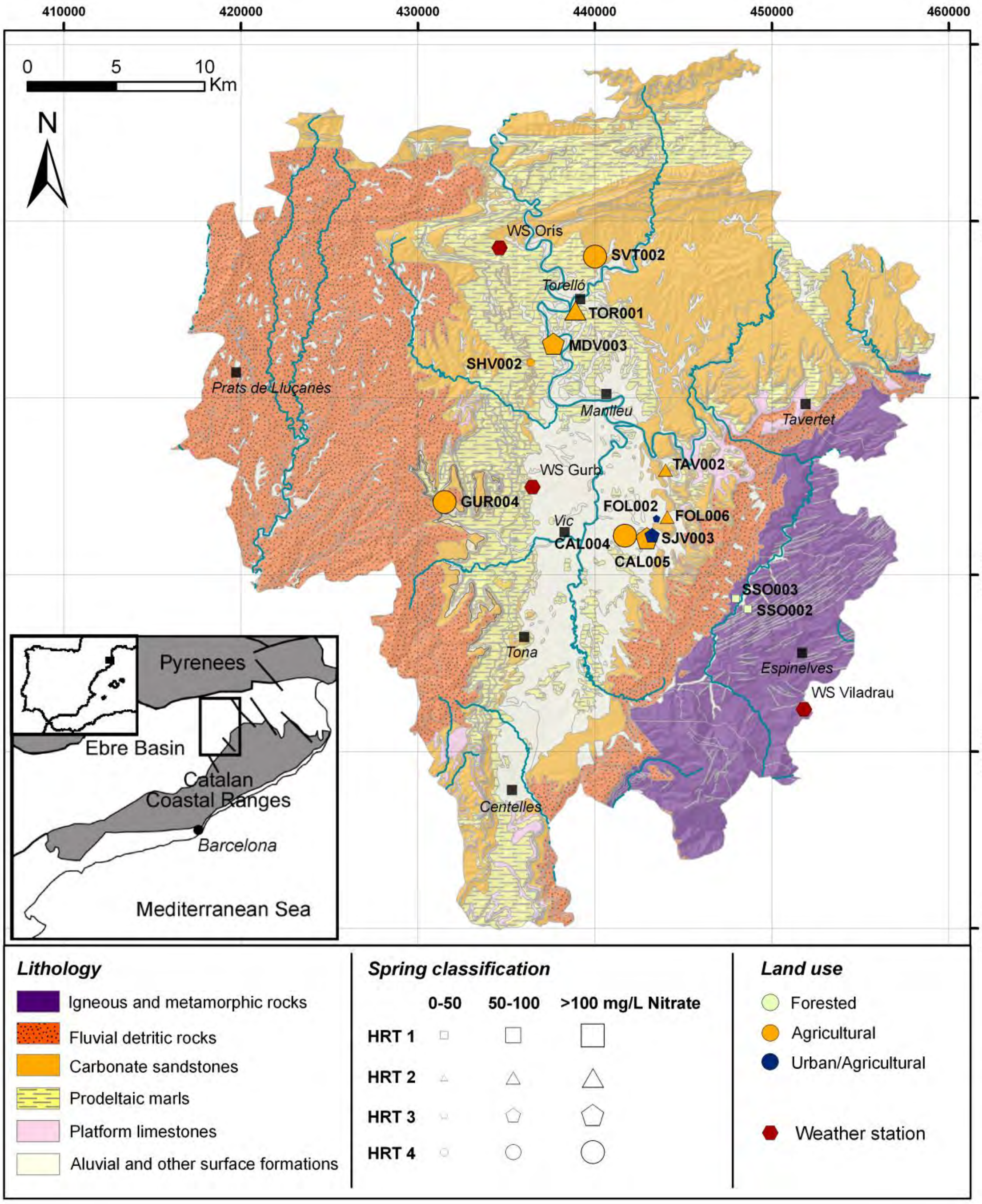


***Figure 3.1** – Map of the geographical and geological setting of springs and the study area, with the locations and characteristics of the springs. Hydrological Response Types (HRT) are described later in section 4.2. Geological formations are mapped according to the main lithology in the area (geological cartography simplified from ICC, 2011). Land use indicates the main type in the recharge area of the springs. Weather stations are also represented in this map.*

The most common crop in the Osona region is wheat, grown on 30% of the total cultivated land (7,219 ha), followed by barley (20%), corn (14%) and sorghum (5%), among other minor crops. In the case of spring wheat and barley, application of slurry as a fertilizer 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 fertilization is from mid-January to July and manure application from January to mid-June. Therefore, the fertilization regime of crops in a given watershed depends on the crop type and the convenience of the farmer. Agricultural practices need to be considered because they may potentially influence nitrate concentration in groundwater.

Menció et al. (2011a) and Otero et al. (2009) studied the pollution sources and the distribution of nitrate in groundwater from local and regional hydrogeological perspectives in the Osona region. According to them, high nitrate concentrations 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 et al. (2004) used $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ to confirm the link between groundwater nitrate pollution and pig manure. Otero et al. (2009), Torrentó et al. (2011) and Vitòria et al. (2008) used environmental isotopes to report the occurrence of natural attenuation processes (denitrification) in this region. Logistic regression and ANOVA analysis identified the importance of land use and geological setting in nitrate pollution in springs (Menció et al., 2011b). These analyzes showed that nitrate pollution was more dependent on land use than on the geological setting of springs.

Regarding nitrate variability in groundwater, Menció et al. (2011a) found that, after a monthly survey of a set of 85 wells during a year in the Osona region, nitrate content showed significant variations. Major nitrate increases were attributed to the alteration of the flow system by groundwater withdrawal that enhanced mixing between resources from different aquifer layers. Geological heterogeneities, as fractures in the confining layers, and the lack of casing in most of the boreholes indicated that nitrate measurements in wells are highly influenced by human factors and that major variability is to be mostly attributed to them and not to natural processes.

The objective of this paper is to characterize the hydrologic and hydrochemical response of springs to rainfall regimes and land uses, with special emphasis on nitrate concentrations, as a means to understand nitrate recharge rates to aquifers (Figure 3.2). Common and/or distinctive patterns among springs, based on their geological setting and hydrologic behavior, are sought in order to explain the migration of nitrogen from its application as fertilizer on the soil to its occurrence as nitrate in springs and eventually in groundwater. These patterns are named Hydrologic Response Types (HRT).

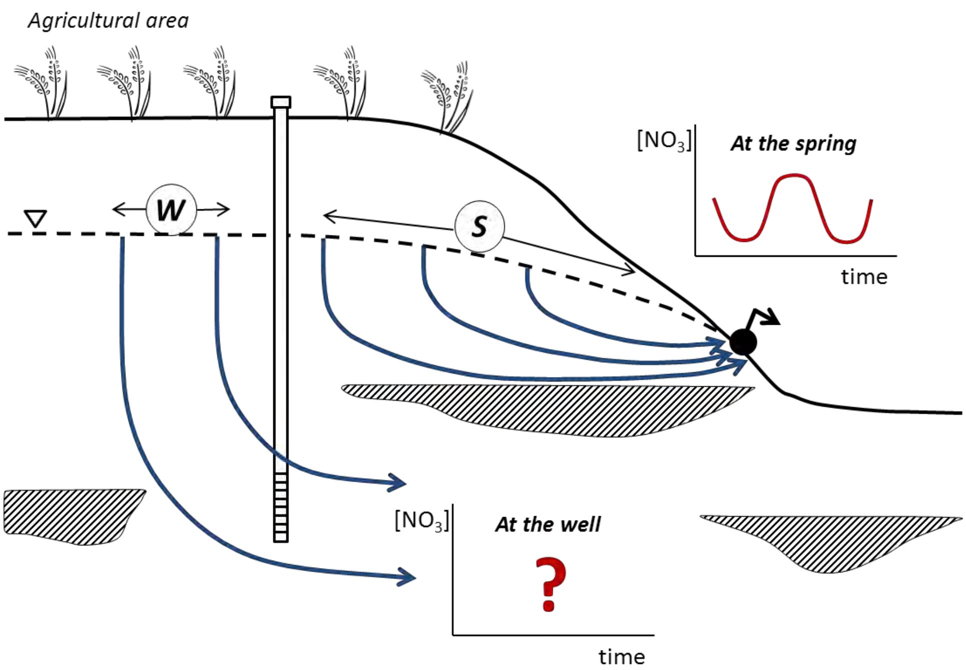


Figure 3.2 – *Conceptual scheme of subsurface flow feeding a spring and the aquifer in a similar geological setting. Geological features, such as clay lenses (cross-hatched), account for the aquifer heterogeneity and determine the position and occurrence of the spring. Recharge areas feeding the spring and the well are referred to as S and W, respectively, in the scheme. The cross-section is not to scale.*

3.2 – GEOLOGICAL AND HYDROGEOLOGICAL SETTING

3.2.1 – Regional geology and hydrogeology

The geological system of the Osona region consists of a sequence of Paleogene sedimentary layers, with a total thickness of approximately 1,500 m, which overlies the Hercynian crystalline rock (igneous and metamorphic) basement. Sedimentary formations are constituted by a thick (≈500 m) basal level of conglomerates, and a later alternation of carbonate formations with calcareous, marl and carbonate sandstone layers (see stratigraphic column and geologic cross-section in Abad, 2001; Menció et al., 2011a) (Figure 3.1). Geomorphologically, it represents an erosional basin created by the drainage network of the Ter River profiting the abundance of silty marl layers in the central area.

Aquifers are located in carbonate and carbonate-sandstone layers whose porosity is due mainly to the fracture network, and occasionally to dissolution. These fractures also affect the marl layers, which consequently act as aquitards and permit a vertical leakage between the aquifers.

Quaternary sediments overlay the rocks mentioned above and support agricultural activity. Alluvial formations are located in the central part of the basin and constitute local aquifers, especially in the Ter River terraces and its floodplain. Other quaternary formations, such as colluvial, eluvial, and mass-wasting deposits, also constitute potential small-scale hydrogeologic units to which the occurrence of springs is frequently related.

3.2.2 – Spring characterization

Springs are categorized according to different variables which help to explain their different hydrological behaviors. Variables such as geology and land use can play an important role in determining the discharge, hydrochemical features and, specifically, the nitrate content in springs.

Springs were selected according to their geological setting and to the predominant land use in their recharge areas, differentiating between forested, agricultural and urban uses (Figures 3.1 and 3.3, Table 3.1). The approximate recharge area of each spring was determined according to its geological context and adjacent topography, and it was used to define the main land use, which finally exerts a control on nitrate recharge to the nearby aquifer system. In this way, we sought to maximize consistency between the characteristics of the recharge area and the subsurface flows that will finally contribute to the spring flow, as well as groundwater recharge (Figure 3.2).

Specifically, springs occur in the following different geological settings (simplified from Menció et al. 2011b):

a) **Springs in crystalline rocks**, related to the Hercynian basement;
b) **Springs in pre-quaternary sedimentary rocks**, related to Paleogene sedimentary rock formations. These are springs associated with fractures in marls or sandstones, or are a result of permeability variations inherent in the layering of the sedimentary formations;
c) **Springs in quaternary sediments**, related to the type of deposit, whether alluvial, colluvial, eluvial or mass-wasting, where the spring occurs. In many cases, springs locate in

the basal geological contact between this unconsolidated sedimentary formation and the underlying sedimentary rocks.

According to classification based on average discharge rate proposed by Meinzer (1923, as cited by Kresic and Stevanovic, 2010), the springs were between the fifth and seventh orders of magnitude, ranging from 0.04 to 1.43 liters per second (Table 3.1).

Figure 3.3 *– Springs and their surrounding areas representative of each Hydrological Response Type (HRT); A: SSO002, Font del Rifà (HRT1); B: FOL006, Font Trobada (HRT2); C: MDV003, Font del Peretó (HRT3); and D: SVT002, Font de Nogueres (HRT4).*

3.2.3 – Meteorology

The study area has a sub-Mediterranean climate with hot summers and cool winters. According to an equally-weighted average from the weather stations at Gurb, Orís and Viladrau (Catalan Weather Service - SMC, 2011; Figure 3.1), the annual mean temperature is 12.6 ºC; and mean precipitation and potential evapotranspiration (using the Thornthwaite equation) are around 715 and 706 mm/year, respectively. Spring and autumn are the rainiest seasons. In summer, potential evapotranspiration is usually twice as much precipitation. During the sampling period of this study (January 2010 – February 2011), frequent rainfall events occurred during the first six months, while such events were sparse in the last seven months (refer to Figures 3.4 to 3.7 for detailed daily rainfall values). Major rainfall events reaching up to 50 mm/day were recorded at the beginning of May and October.

3.3 – METHODOLOGY

Aware of nitrate pollution problems in the region and the deterioration of spring water quality, the local authority (Consell Comarcal d'Osona) started a sampling program in 2004 with the aim of monitoring, twice a year, nitrate concentration in springs in the Osona region. This dataset, which contained about 130 springs, was used to describe spring vulnerability to nitrate pollution depending on geological setting and land use in the recharge area (Menció et al., 2011b). For the present study, 13 springs out of this large database were selected for a periodic survey over one year. These springs are representative of each geological setting and land use category.

3.3.1 – Field sampling and chemical analysis

Detailed sampling of 13 selected springs was conducted to monitor over time the variability of nitrate concentration together with other parameters such as spring flow, electrical conductivity (EC), pH and water temperature. Springs were sampled every two weeks from January 2010 until February 2011. In total, they were sampled 27 times. In the case of CAL004, the nitrate concentration and electrical conductivity of stream water from a nearby creek were periodically analyzed to check for any differences between stream and spring water. Two extensive hydrochemical analyzes, including major hydrochemical components, were conducted in two sampling campaigns (February 2010 and February 2011).

Electrical conductivity and temperature were determined in the field with a Crison *CM35* portable conductivity meter with a temperature measurement capability (accuracy EC ≤ 0.5%; temperature ≤ 0.2 ºC). pH was also measured *in situ* with a WTW-330i pH meter (accuracy ≤ 0.0005 pH) and discharge was measured with a stopwatch and a calibrated container. Water samples were filtered, acidified for cation analysis, and stored and transported to the laboratory under cooled conditions. Once there, samples were filtered through a 0.20 micron nylon filter and stored at 4ºC before being analyzed. Nitrate and nitrite content were analyzed by ion-exchange chromatography while ammonium was analyzed directly (without filtering) by steam distillation. Anion analysis was performed by capillary electrophoresis with previous micro filtration (0.22 µm), and alkalinity was determined using the Gran titration. Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Geochemical modeling (PRHREEQC) was used to calculate carbon dioxide partial pressure (P_{CO2}) and the calcite saturation index.

3.3.2 – Exploratory statistics and geostatistical analyzes

Exploratory data analysis is performed in order to describe patterns and to investigate the relations between the different variables from a hydrologic perspective. Basic statistics for all variables were calculated using an SPSS 15.0 statistical package.

Springs were categorized on the basis of the fluctuation of discharge, EC and nitrate content over time in accordance with their response to rainfall. The evolution of these variables along the sampling period was plotted together in Figures 3.4 to 3.7. Common patterns of these variables in the springs meant they could be classified in four different groups, called here Hydrological Response Types (HRT). This classification system will be used later in the paper. Geological setting and land use variables are considered in the interpretation of the different behaviors (section 3.4.2).

The mass load of nitrate in spring water was calculated to estimate how much of it was discharged at each survey during the sampling campaign. The total nitrate mass load was summed for each spring, and the accumulated load was normalized to the final mass load value to allow comparison among springs.

Geostatistical analysis of discharge and nitrate time-series provides an additional insight into their temporal evolution. Although geostatistics have been used for the analysis of discharge (e.g., Jalbert et al., 2011) and hydrochemical data time-series (Zhang and Schilling, 2005; Schilling, 2009), it is not a usual approach to characterize temporal data sets. In this paper, variograms are used with the aim to objectively compare different temporal trends, and to describe how temporal continuity changes as a function of time lags. This analysis lays on the experimental semi-variogram (hereafter referred to as the variogram) as calculated from the data, and a variogram model fitted to the data (e.g., Isaaks and Srivastava, 1989; Kitanidis, 1997, among other textbooks). An estimate of the experimental variogram is given by:

$$\gamma(h) = \frac{1}{2}\sum_{i=1}^{N(h)} \frac{\left[Z(t_i + h) - Z(t_i)\right]^2}{N(h)}$$

where γ is the variogram, Z is the value of the variable of interest at time (t), h is the time lag, and N is the number of data pairs at each lag.

The variogram model is chosen by matching the shape of the curve of the experimental variogram to given mathematical functions (Barnes, 2003). The variogram parameters (sill, range and nugget values) and the fitted model were calculated using a Surfer v9 software package, developed by Golden Software Inc. (2010).

Experimental variograms were performed for temporal discharge and nitrate data at given locations in the time direction (unidirectional). To evaluate the occurrence of a drift that governs temporal evolution, the correlation coefficient between the reference function (fitted variogram model) and the potential drift function (i.e.: a polinomy usually of first degree) was estimated. In those cases that the correlation coefficient was higher than 0.5, data were detrended to eliminate much of the redundant (drift-related) variability in the experimental variogram. A spherical model was used by default to fit the resulting variograms. A Gaussian model was also used if so indicated by the shape of the experimental variogram.

Conductivity variograms are not shown here as most of the variograms had severe drifts due to the rise in EC after the summer season, which overruled the stationarity assumption and masked EC time variability. As their contribution was poor, they are not included in this paper.

3.4 – RESULTS

3.4.1 – Hydrochemistry of the springs

Mean nitrate concentration in springs ranged from 8 to 391 mg/L (Table 3.1). In only 4 out of 13 springs was the mean nitrate concentration below the threshold for drinking water (50 mg/L), while average nitrate levels were above 200 mg/L in four cases. The highest concentrations were in springs located in sedimentary formations (groups B and C) with agricultural activity in their recharge areas, while the lowest values were in springs found in crystalline rocks (group A) and in forested areas.

Electrical conductivities varied from 407 µS/cm at the most pristine spring, to 1,343 µS/cm at the most polluted in terms of NO_3^-. EC also depended on the geology where the spring was located. For instance, lower EC values were found in the eastern part of Plana de Vic, which is associated with the occurrence of carbonate sandstones formation (e.g. FOL002, FOL006 and TAV002; Figure 3.1). Furthermore, several springs showed an increase in EC in the last semester of the sampling campaign, fact that will be addressed in the discussion. Mean pH values ranged from 6.9 to 7.4. There was a relatively uniform temperature regime in most spring waters throughout the year, varying by only a few decidegrees in line with air temperature, but in a lower range. Average water temperatures ranged from 10.7 to 14.3ºC.

HRT	Spring code	Spring name	n	Discharge (L/s)		EC (uS/cm)		NO_3^- (mg/L)		NO_3^- T.M.L. (kg)	pH		Water temp. (ºC)		Geological type	Land use
				ME	SD	ME	SD	ME	SD		ME	SD	ME	SD		
1	**SSO002**	F. del Rifà	26*	0.162	0.03	407.4	34.4	10.3	1.0	56	7.0	0.1	12.7	0.6	A	forested
	SSO003	F. dels Peons	26*	0.051	0.03	658.3	108.6	7.9	1.4	15	7.4	0.1	10.7	1.1	A	forested
2	**FOL006**	F. Trobada	27	0.343	0.06	609.9	51.6	90.4	9.3	1084	7.1	0.1	13.0	0.5	C	agricultural
	TAV002	F. del Pujol	27	1,429	0.42	625.3	50.1	67.3	5.1	3179	7.2	0.1	12.3	0.6	C	agricultural/forested
	TOR001	F. dels Ocells	26*	0.042	0.01	759.6	71.4	166.2	21.7	228	7.2	0.1	12.9	0.7	B/C	agricultural
3	**CAL005**	F. Altarriba	27	0.053	0.02	957.3	74.2	252.4	28.3	483	7.2	0.1	12.0	1.8	C	agricultural
	FOL002	F. del Glaç	27	0.043	0.04	544.0	36.5	38.2	4.8	53	7.3	0.3	12.6	1.1	C	urban/agricultural
	MDV003	F. del Peretó	27	0.701	0.33	1.080.0	71.9	222.1	19.6	5447	7.0	0.1	14.0	0.7	C	agricultural
	SJV003	F. d'en Titus	26**	0.145	0.10	847.0	42.7	55.7	9.5	285	6.9	0.1	13.9	1.5	B/C	urban/agricultural
4	**CAL004**	F. de la Gana	27	0.542	0.65	1.134.2	91.3	280.6	83.1	6129	7.0	0.1	13.2	0.9	C	agricultural
	GUR004	F. Salada	27***	0.107	0.08	1.343.3	75.6	390.9	26.1	1425	7.1	0.2	13.2	0.5	B	agricultural
	SHV002	F. de la Sala	27	0.054	0.07	676.1	89.0	42.5	12.6	59	7.1	0.1	11.9	1.5	C	agricultural/forested
	SVT002	F. Nogueres	27	0.358	0.30	803.3	83.3	107.2	16.0	1278	7.2	0.1	14.3	0.4	B	agricultural/forested

HRT: Hydrological Response Type; ME: Mean; SD: Standard Deviation; T.M.L.: Total Mass Load.

Geological type: A: crystalline rocks; B: pre-quaternary sedimentary rocks; C: quaternary sediments.

* Nitrate concentration from one campaign (July'10) was not used in the statistics because of analytical error.

** Due to weather conditions and flooding of the spring area, it was not possible to monitor this spring in one of the campaigns (3/5/2010).

*** High discharge values at GUR004 could not be accurately measured in five sampling campaigns. Discharge for these campaigns is thus an approximate estimate of the actual values.

Table 3.1 – *Spring typology and basic statistics for the physicochemical parameters of spring water samples over the 27 campaigns.*

HRT	Spring code	EC (µS/cm)	pH	Water T (ºC)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	NO_2^- (mg/L)	NH_4^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Calcite SI	pCO_2 (atm)
February 2010																
1	SSO002	373	7.01	13.1	217.2	14	31.2	9.6	< 0.2	3.53	57.7	15.8	17.6	1.4	-0.52	0.0159
	SSO003	604	7.18	9.9	183.0	15	162.0	7.9	< 0.2	3.60	110.0	19.2	17.2	1.8	-0.23	0.0094
2	FOL006	563	7.06	12.6	387.5	39	17.7	88.6	< 0.2	2.34	143.0	11.3	7.7	1.6	0.09	0.0245
	TAV002	589	7.11	12.1	369.9	53	25.9	68.5	< 0.2	3.99	134.9	17.6	11.4	2.0	0.09	0.0210
	TOR001	671	7.14	12.6	330.9	78	32.3	133.9	< 0.2	3.02	128.4	32.4	12.6	4.7	0.03	0.0172
3	CAL005	960	7.08	10.3	309.4	86	114.0	218.1	< 0.2	3.34	217.5	19.7	21.5	3.6	0.10	0.0189
	FOL002	511	7.18	11.9	255.7	115	15.5	42.9	< 0.2	4.40	123.7	9.9	11.1	< 1	-0.04	0.0126
	MDV003	1037	6.96	13.5	419.2	142	77.0	214.9	< 0.2	3.19	195.3	47.6	38.7	11.2	0.08	0.0313
	SJV003	828	6.86	13.0	389.9	181	65.0	71.2	< 0.2	4.14	210.8	14.0	33.5	< 1	0.01	0.0378
4	CAL004	1106	7.03	12.9	359.9	92	126.0	284.5	< 0.2	3.20	247.9	30.5	38.5	6.8	0.18	0.0229
	GUR004	1244	7.11	13.5	423.6	129	144.0	353.5	< 0.2	3.19	261.1	50.5	36.9	4.0	0.33	0.0217
	SHV002	689	7.12	10.8	400.2	82	50.0	51.9	< 0.2	2.97	138.6	27.5	15.8	16.8	0.10	0.0228
	SVT002	778	7.07	14.1	394.8	145	48.0	84.8	< 0.2	3.43	161.6	30.6	16.8	19.4	0.13	0.0232
February 2011																
1	SSO002	437	7.22	11.8	231.8	14	42.0	9.4	< 0.2	1.93	64.0	17.2	18.8	1.5	-0.26	0.0107
	SSO003	811	7.56	9.3	173.7	14	211.0	7.1	< 0.2	2.21	133.7	23.0	18.8	2.0	0.18	0.0037
2	FOL006	666	7.25	12.5	358.7	39	22.5	94.7	< 0.2	2.24	151.2	11.8	8.0	1.5	0.27	0.0146
	TAV002	670	7.30	11.7	388.4	50.0	26.6	68.3	< 0.2	1.87	139.1	17.8	11.5	2.0	0.30	0.0144
	TOR001	771	7.31	13.1	328.9	85.0	39.3	146.2	< 0.2	2.06	144.6	34.3	13.7	5.0	0.24	0.0113
3	CAL005	995	7.49	9.7	334.8	85	113.0	209.9	< 0.2	2.22	213.8	19.3	21.6	3.1	0.52	0.0080
	FOL002	570	7.76	11.0	270.8	97	14.7	38.7	< 0.2	2.20	127.2	10.1	11.1	< 1	0.56	0.0035
	MDV003	1177	7.11	13.5	451.4	139	77.0	252.3	< 0.2	2.43	202.3	48.9	37.7	11.7	0.27	0.0237
	SJV003	830	7.09	12.0	403.1	131	47.0	45.6	< 0.2	2.40	189.5	13.0	29.3	< 1	0.21	0.0237
4	CAL004	1032	7.19	12.2	372.8	71	107.0	168.0	< 0.2	1.74	197.1	27.0	33.8	5.2	0.28	0.0170
	GUR004	1376	7.25	13.5	415.3	129	141.0	361.7	< 0.2	2.83	256.0	50.5	36.9	4.6	0.45	0.0154
	SHV002	731	7.25	10.0	406.3	63	40.0	47.6	< 0.2	2.41	135.4	26.3	15.0	15.8	0.23	0.0175
	SVT002	869	7.21	14.7	387.0	106.0	56.0	106.6	< 0.2	2.20	163.3	29.2	18.6	16.8	0.28	0.0162

Errors based on % ionic balance lay in the range of ± 5%.

Table 3.2 – *Hydrochemical results of the sampling campaigns of February 2010 and February 2011.*

Hydrochemically, springs were of the calcium-bicarbonate water type, except in one case (SSO003) which was a calcium-chloride type. Spring hydrochemistry is similar to the one of the wells and consistent with the geochemistry across the Osona region (Menció et al., 2011a).

In general terms, anion and cation concentrations were quite constant in the sampling campaigns of both February 2010 and February 2011, but there were changes in some ion concentrations (Table 3.2). In most springs, an increment or a decrease in nitrate concentration involved, respectively, a rise or a fall in chloride content and other cations, such as calcium and sodium, which rebalance the system. This fact is supported by the high positive correlation between nitrate content and chloride (r^2 = 0.88), calcium (r^2 = 0.86) and sodium (r^2 = 0.69). However, the low correlation between SO_4^{2-} and nitrate (r^2 = 0.49) suggest that since there are no evaporite rocks in the study area, groundwater SO_4^{2-} is assumed to be related to the oxidation of disseminated pyrite, as mentioned by Vitòria et al. (2008).

3.4.2 – Discharge, electrical conductivity and nitrate time series

For ease of reference, the characteristics of the different Hydrological Response Type groups are summarized in Table 3.3. Figures 3.4 to 3.7 represent the time trends of spring discharge, EC and nitrate content over the 27 sampling campaigns, and average daily rainfall data from the Osona region. pH values and water temperature are not shown as they were constant throughout the year.

HRT	Discharge	EC	Nitrate	Responsive to rainfall	Geological type	Land use	Springs
1	Uniform	Uniform with increasing trend	Uniform	No	A	Forested	SSO002, SSO003
2	Uniform	Uniform with increasing trend	Uniform	No	C	Agricultural / Forested	FOL006, TAV002, TOR001
3	Variable	Uniform with increasing trend	Variable	Yes	C	Agricultural / Urban	CAL005, FOL002, MDV003, SJV003
4	Variable	Variable	Variable	Yes	B, C	Agricultural / Forested	CAL004, GUR004, SHV002, SVT002

Table 3.3 – *Main features of each variable within each Hydrological Response Type (HRT).*

The features of each Hydrological Response Type (HRT) shown in Figures 3.4 to 3.7 are:

- ***Hydrological Response Type 1 (HRT 1)***; Figure 3.4: these springs are in forested areas and present low (< 11 mg/L) nitrate concentrations that are uniform over time. They are both located in crystalline rocks (group A), unsuited to agricultural activity, which means that there is an absence of fertilizer application. In the case of SSO002, discharge, EC and nitrate content remain fairly constant throughout the year. SSO003 shows an EC increment, which might be associated with an unusual occurrence of chloride attributable to road salt pollution. Small fluctuations in its discharge can be also observed.

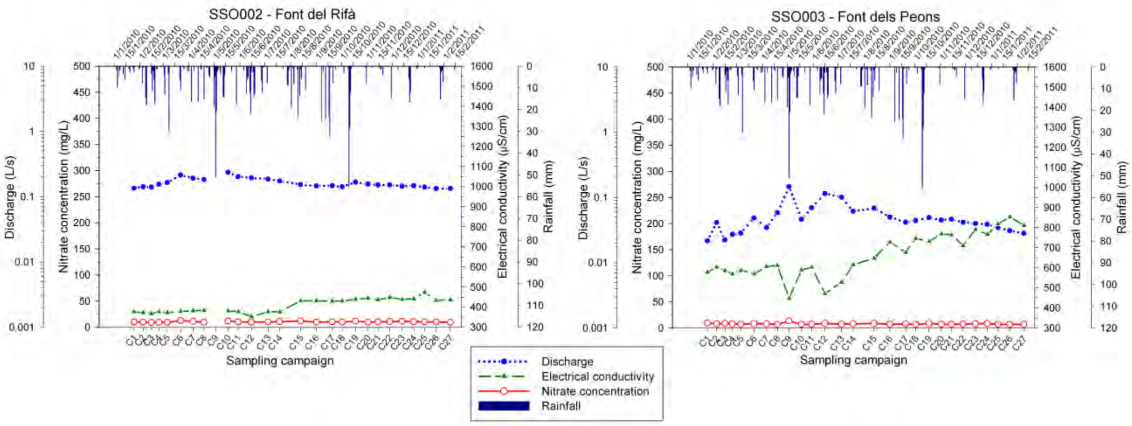


***Figure 3.4 –** Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 1 (HRT 1).*

- ***Hydrological Response Type 2 (HRT 2)***; Figure 3.5: different from HRT1, the land use of the recharge area of these springs is mainly agricultural, but forested land is also found. This could be the reason why nitrate content is moderately high (average concentration 65-166 mg/L), but not as high as in other springs exclusively in agricultural areas (HRT3 and HRT4; Table 3.1). These springs drain widespread surface deposits (alluvial, colluvial and eluvial), usually with large hydraulic conductivity values (group C). They are characterized by a relatively uniform discharge, EC and nitrate content over time with little influence from rainfall.

- ***Hydrological Response Type 3 (HRT 3)***; Figure 3.6: two different nitrate concentration ranges can be observed here. Nitrate content varied moderately and had very high values (above 200 mg/L) in CAL005 and MDV003, both surrounded by areas of intensive agriculture. On the other hand, FOL002 and SJV003, located near urban areas with less influence from cultivated crops, had lower and steadier nitrate concentrations (averaging from 38 to 56 mg/L) over time. Most of these springs are located in quaternary sedimentary formations, associated with alluvial or colluvial sediments (group C). Springs occur at the geological contact with the underlying, less permeable formation, usually marls or sandstones. Discharge trends show the influence of major rainfall periods, yet specific flow peaks after rainfall events were not always recorded. Discharge decreased progressively during low rainfall periods, as seen in the last three months of the monitoring campaign. In contrast to discharge trends, EC generally increased.

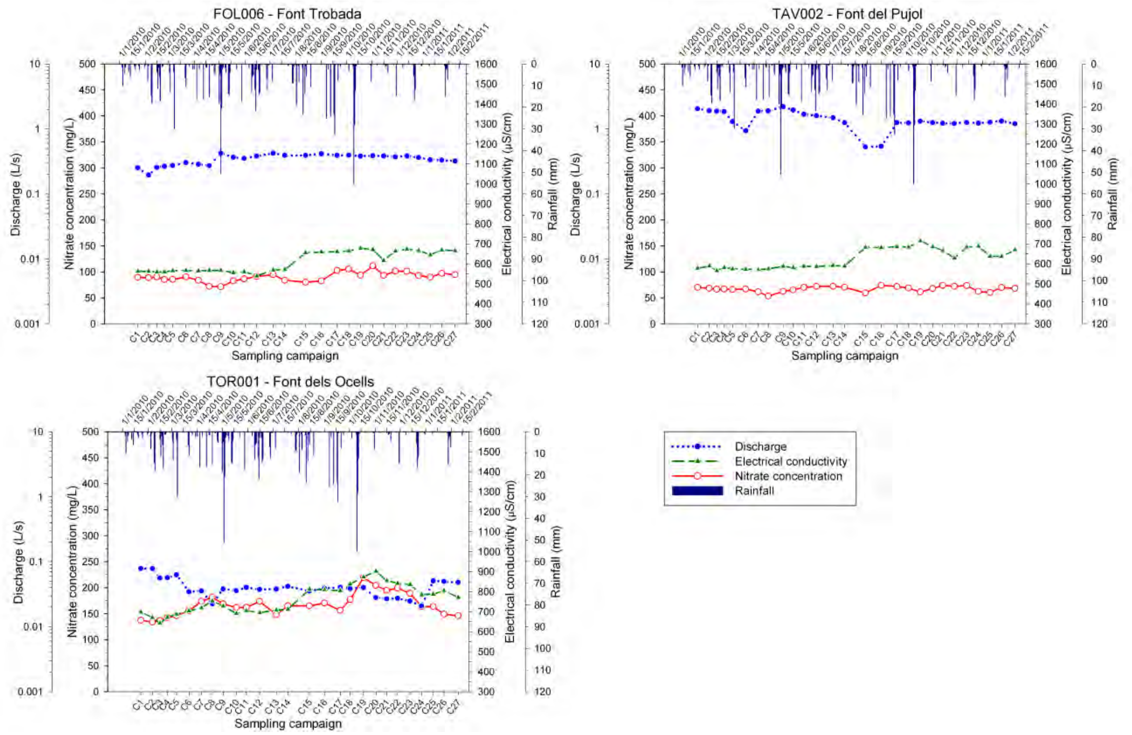


Figure 3.5 – *Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 2 (HRT 2).*

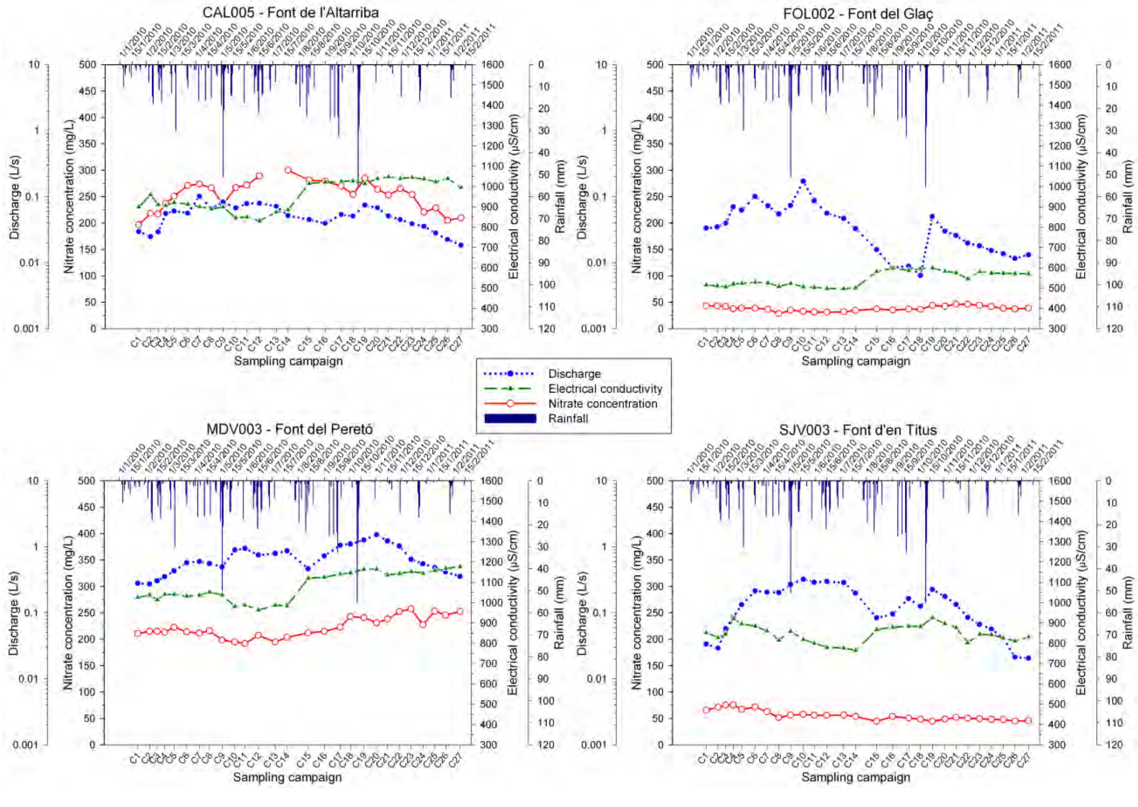


Figure 3.6 – *Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 3 (HRT 3).*

- ***Hydrological Response Type 4 (HRT 4)***; Figure 3.7: these springs are found in pre-quaternary and quaternary sedimentary formations (groups B and C) and nitrate concentration is related to the predominance of cultivated crops in the recharge area. Discharge varies significantly immediately or shortly after rainfall events and EC behaves similarly. When no rainfall is reported, these variables remain fairly stable or decrease slightly. However, no clear relationship can be observed between nitrate content and discharge and EC evolution, except in the case of spring CAL004 which, as it was afterwards determined, is influenced by stream water contributions in its headwaters.

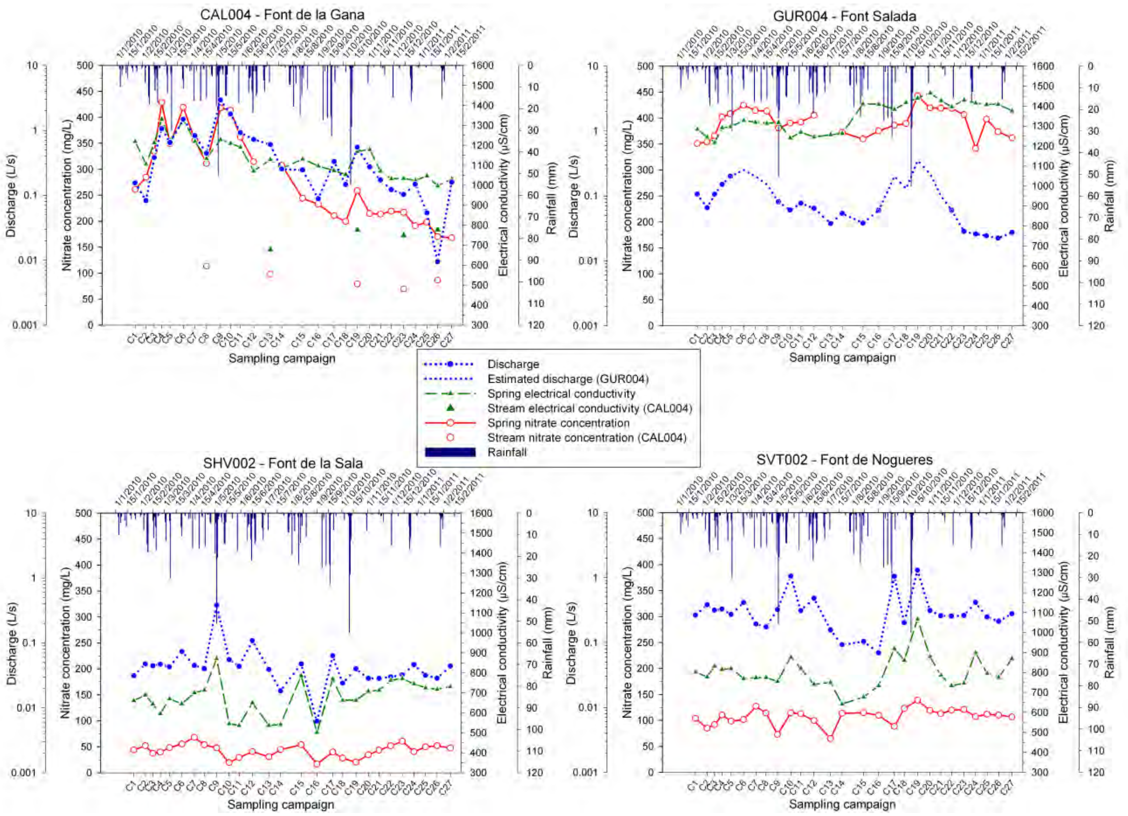


Figure 3.7 *– Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 4 (HRT 4). EC and nitrate data for the stream located near CAL004 are also shown. Estimated discharge, based on field observations, for non-gauged months at GUR004 is indicated by a broken line without symbols.*

3.4.3. Nitrate accumulated mass load

The accumulated mass load of nitrate in spring water was calculated in order to illustrate how nitrate outputs vary over time. Total mass values at the end of the sampling campaign are given in Table 3.1, and the normalized mass evolution for each spring, grouped according to its HRT, is plotted in Figure 3.8.

Each HRT group has its particular response to a common rainfall regime. Springs in groups HRT1 and HRT2 show an almost constant slope in the progress of their accumulated mass load, with virtually no influence from the rainfall regime. This corroborates the trends shown in the discharge and nitrate time series (Figures 3.4 and 3.5). In these two groups, 50% of the total nitrate load is reached approximately in the middle of the sampling period, between June and July 2010. This parameter is an indicator of the temporal continuity of the nitrate mass load.

HRT3 springs show smooth discharge variations and a continuous decrease in their outflow between the main rainfall events. Except for MDV003, they are most sensitive to the intensive rainfall in May, and their mass load appears less influenced by the rainfall events recorded in the autumn. Then, the uniform mass load of nitrate is only modified by large alterations to the flow system. In the specific case of MDV003, the increase in its nitrate content from September reversed the effect of discharge diminution and led finally to an increase in the slope of the accumulated mass load curve. In the springs in this group, 50% of the nitrate mass load is reached earlier, in May, except for MDV003, when it is in September 2010.

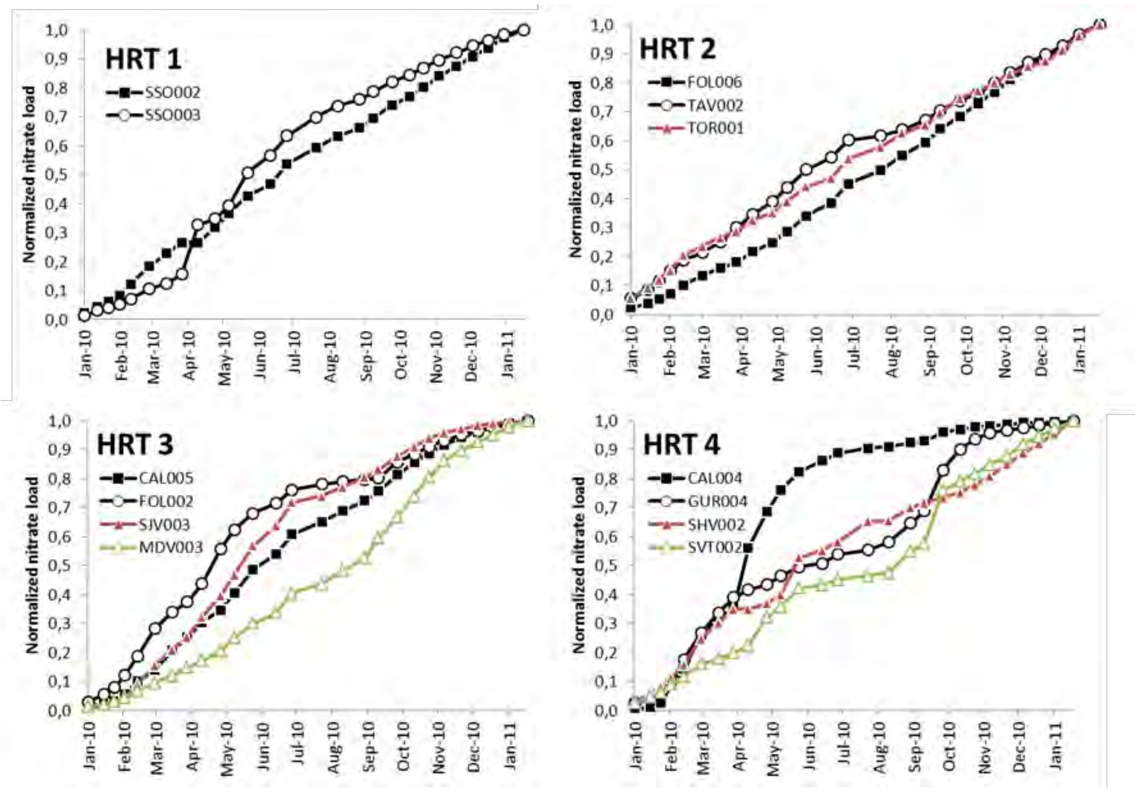


Figure 3.8 – *Normalized nitrate accumulated mass load for each HRT.*

Springs highly sensitive to rainfall events, like those in the HRT4 group, evince changes in their accumulated mass load evolution. Nonetheless, an averaged continuous slope can still be devised for these springs. CAL004, however, behaves differently due to the influence of stream water. The majority of its loading occurs prior to the major rainfall event in May and its discharge is higher during spring time (nitrate stream mean value is 90 mg/l, see Figure 3.7). In April 2010, this spring already has half of its total nitrate mass load. Two other springs in this group reached this mass-percentage between May and June, and SVT002 reached it in late August.

3.4.4. Geostatistical analysis

Geostatistical time-variability was studied to reveal how much control hydrological processes have over the rate of discharge and nitrate content during the spring time-series (Figures 3.9 and 3.10). Variogram model parameters for discharge and nitrate are presented in Table 3.4.

Variable	HRT	Spring code	CV	Model	Detrended	Nugget	Range	Sill
DISCHARGE	1	SSO002	0.16	Spherical	no	0	9.69	0.001
		SSO003	0.55	Spherical	no	0	8.23	0.001
	2	FOL006	0.18	Spherical	no	0	18.05	0.006
		TAV002	0.29	Spherical	no	0.01	5.75	0.194
		TOR001	0.35	Spherical	no	0	6	0.000
	3	CAL005	0.39	Spherical	no	0	7.40	0.001
		FOL002	0.82	Spherical	no	0	10.01	0.001
		MDV003	0.47	Spherical	no	0	8	0.124
		SJV003	0.64	Spherical	no	0	10.74	0.013
	4	CAL004	1.21	Spherical	no	0.12	8.69	0.405
		GUR004	0.68	Spherical	no	0	4.80	0.007
		SHV002	1.25	Spherical	no	0	1.39	0.005
		SVT002	0.82	Spherical	no	0	0.99	0.095
NITRATE	1	SSO002	0.09	Spherical	no	0	1.47	0.94
		SSO003	0.17	Spherical	no	0	0.99	2
	2	FOL006	0.10	Spherical	no	30	9.20	70
		TAV002	0.08	Spherical	no	0	2.13	28.40
		TOR001	0.13	Spherical	no	0	6.30	477
	3	CAL005	0.11	Spherical	no	0	9.80	1035
		FOL002	0.13	Spherical	no	0	9.44	34
		MDV003	0.09	Gaussian	no	44.57	8.86	591
				Spherical	yes	9.86	8.56	211
		SJV003	0.17	Gaussian	no	18.89	27.47	485.60
				Spherical	yes	7.90	6.46	19.24
	4	CAL004	0.29	Gaussian	no	1140	13.22	14940
				Spherical	yes	786.60	7.74	2121
		GUR004	0.06	Spherical	no	130	4.80	636.10
		SHV002	0.30	Spherical	no	68.70	5.30	124.70
		SVT002	0.15	Spherical	no	143	1.59	266.10

HRT: Hydrological Response Type; CV: Coefficient of Variation.

Table 3.4 – *Basic statistics of the discharge and nitrate data and variogram model parameters.*

Discharge variograms

The discharge variograms reflect the flow patterns of each of the hydrological response types (Figure 3.9). Those springs that show a uniform, smoothly varying discharge throughout the entire study period (HRT1, HRT2), display a progressive and continuous increment in their variogram value over time till they reach the sill, or the variance in the data series. Moreover, those springs included in the HRT3 group, which have larger outflow variations, behave similarly. Range values for the HRT1 series (8 to 9 sampling campaigns, i.e. from 4 to 5 months) and for HRT3 (7.5 to 11 sampling campaigns, i.e. from 3.5 to 5.5 months) are greater than those for the HRT2 series (6 sampling campaigns, i.e. about 3 months). This indicates a longer time span until data attains its expected variability. Spring FOL006 (HRT2 group) constitutes an exception, as it has a very wide range (18 sampling campaigns, i.e. 9 months), although a small sill, as a result of the decline in steadiness of its discharge during most of the study period.

Springs classified in the HRT4 group are characterized by a highly variable discharge related to rainfall episodes, and therefore have small ranges (from 1 to 5 sampling campaigns, i.e. from 0.5 to 2 months). CAL004 is again an exception. In this case, the wider range of the variogram and its nugget can be attributed to the influence of surface recharge upon the spring outflow. Springs in HRT4 are also characterized by a hole-effect that appears after nine sampling campaign lags. Such a hole-effect is also evident in other hydrologic response patterns, clearly in spring FOL002 and MDV003 (from HRT3), and hinted at in some others. It affects those springs where it was observed that rainfall events had a major influence on discharge.

Within the HRT4 group, variograms for springs SHV002 and SVT002 show almost a pure nugget effect, that is, a random field with small-scale variability at a scale shorter than, or close to, the separation time between measurements. It is evident that discharge records in both springs are stationary, and that their variability even at short lag times is set near their variances. This indicates discharge is sensitive to rainfall inputs.

Nitrate variograms

Nitrate variograms for the HRT1 springs show a uniform variability for any lag time (Figure 3.10). Spherical variograms were used, with very small ranges of about a month (from 1 to 2 sampling campaigns), and a sill value very close to the sample variance. These experimental variograms could actually be represented by a pure nugget model. To the naked eye, the two nitrate series may look almost uniform and appear to be characterized by little variance around the mean value. Nevertheless, geostatistical analysis depicts this small variability in the variogram. From a hydrological perspective, nitrate content is steady, with a minor variability that persists uniformly over time.

Springs classified as HRT2 exhibit greater diversity of nitrate variogram shapes. For instance, FOL006 and TAV002 show steady nitrate records with low variances and coefficients of variation. FOL006 and TOR001 variograms show a correlation length, or range, of about 3 to 4.5 months (from 6 to 9 sampling campaigns). TOR001 has greater variability and its marked hole-effect reflects a nitrate response to the October rainfall episode which is replicated neither in the discharge record nor in its variogram. The hole-effect, however, is not as much clearly reproduced in nitrate variograms as it is in discharge. Within the same group, TAV002 has a very small range, thus indicating short temporal nitrate variability. This is further evidence for interpreting uniform nitrate content in the outflow as being a result of homogenized nitrate inputs within the aquifer.

Springs grouped in HRT3 show two ranges of nitrate content, but their discharge and conductivity patterns contain common features that mean they should be classified together. In this group, nitrate variability is not associated with the nitrate mean value. For instance, CAL005 and FOL002, with mean nitrate content of 252±28 and 38±5 mg/L respectively, have similar ranges of 7-9 sampling campaigns (about 4.5 months) in the modeled variograms, and their sills are in agreement with nitrate variances.

On the other hand, a drift function was identified in nitrate variograms for springs MDV003 and SJV003, and the trend was removed. The random residuals from the drift function show stationary behavior with similar ranges of 3.5 - 4.5 months (6.5 - 8.5 sampling campaigns).

Finally, HRT4 springs are characterized by both discharge and nitrate variability and thus show the highest variances and coefficients of variation. The short-scale variability observed in their nitrate evolution, which indicates some sensitivity to the rainfall regime, although there is not always a clear agreement between discharge and nitrate variations (Figures 3.7 and 3.8), is evidenced by the small range of the modeled variograms. Again, the relationship between stream leakage and spring behavior in CAL004 produces a continuous decline in the spring nitrate content, presumably related to the stream nitrate decrease that defines a trend in the nitrate series. The hole-effect shown by GUR004 is consistent in both discharge and nitrate variograms and, in this case, it reflects a common trend of both variables with respect to the rainfall inputs.

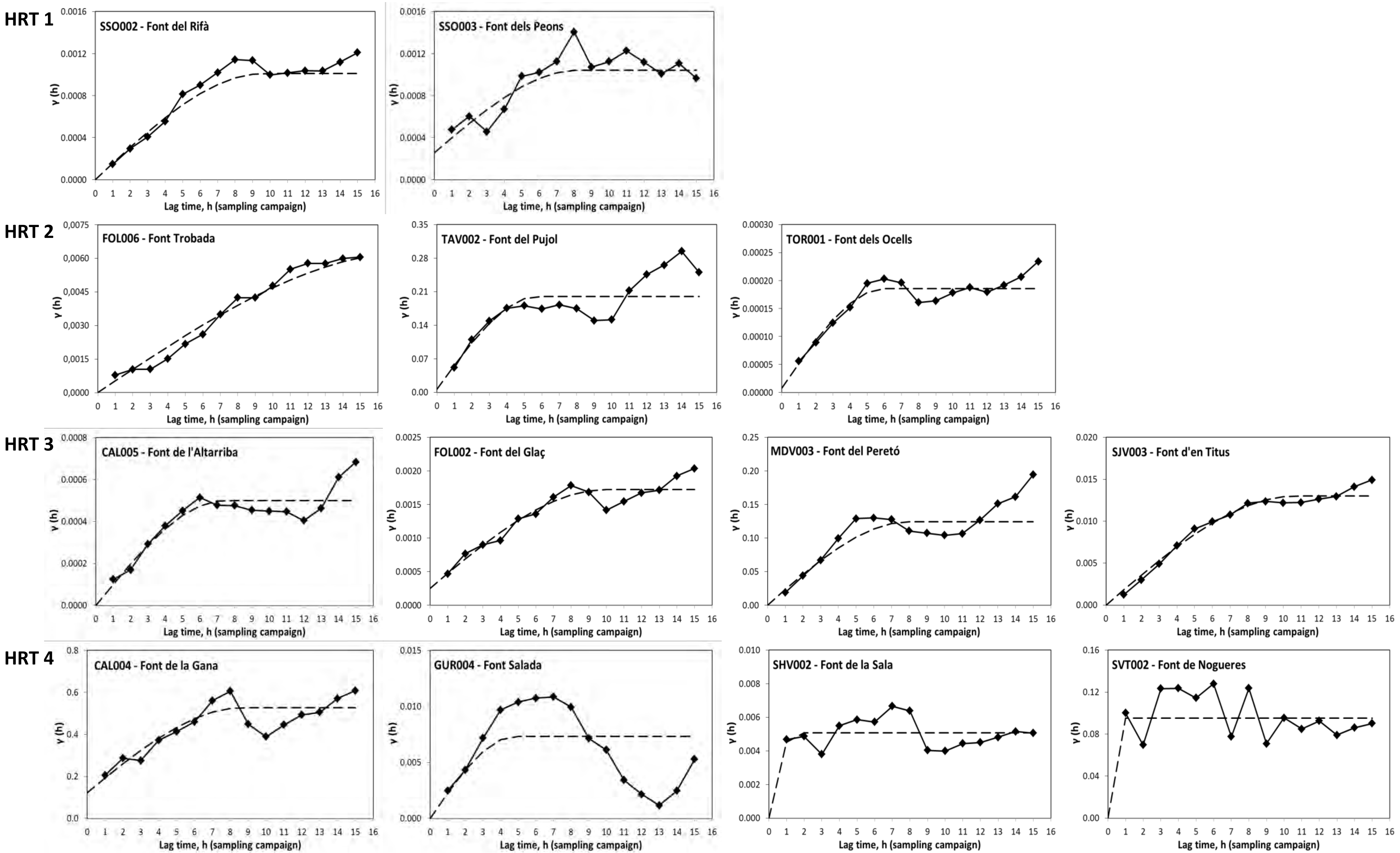


Figure 3.9 – *Experimental and fitted variograms for discharge data. The solid line represents the experimental variogram and the dashed line is the model variogram.*

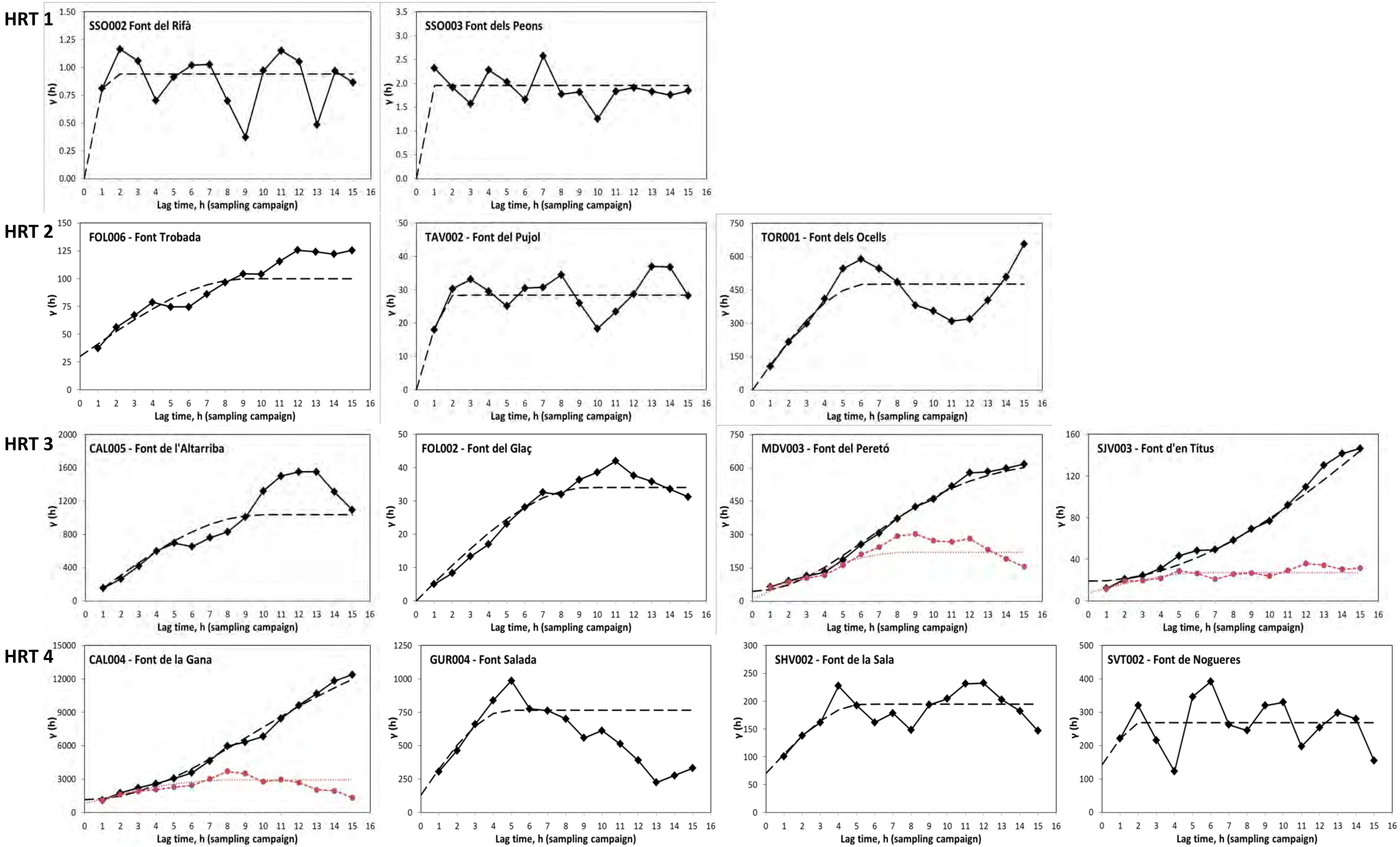


Figure 3.10 – *Experimental and fitted variograms for nitrate data. The solid line represents the experimental variogram and the dashed line is the model variogram. The red line represents the experimental and model variogram for detrended data.*

3.5 – DISCUSSION

Analysis of discharge, EC and nitrate content time-series in the Osona springs distinguishes between different hydrological responses in a common rainfall regime. The study of these variables explains the characteristics of subsurface fluxes and illustrates the recharge that takes place in shallow aquifers with similar hydrogeological characteristics. Spring hydrology is thus indicative of the water quality of groundwater and how nitrate concentration evolves in the subsurface.

In particular, EC changes in spring water over time indicate water-rock interaction and dilution processes along its pathway from the recharge area to its output in the spring. Uniform rainfall in the first six months of the survey allowed dilution of the components present in soil water, resulting in lower EC values in the springs. In contrast, following an increase in EC in most springs between July and August after a month with little or no rain, values remained more or less constant till the end of the monitoring campaign. This rise in EC, together with an increase in some specific ions, can be explained by the sparse rainfall events recorded during the last seven months of the survey. As a result, there was less infiltration and the discharge decreased in several springs, which is attributed to lower hydraulic gradients within the subsurface unconfined aquifers that feed the springs. This allowed more time for water-rock interaction to occur, and also limited dilution. These changes in EC depend on whether spring discharge is only determined by the draining of surface deposits (shallow flow lines) or whether flow paths from the underlying formations also contribute to its outflow (deeper flow lines).

As shown in the temporal evolution of spring hydrochemistry (Figures 3.4 to 3.7), no significant changes in nitrate content related to rainfall events or fertilization regimes over the sampling period were observed. This observation points to a homogenization of the nitrate concentration in the subsurface from the spring recharge areas, where crop fertilization occurs, to the spring location.

Land use, geological setting and rainfall events are all factors which determine the discharge as well as the hydrochemical characteristics of spring water. But they are not relevant to nitrate evolution in springs or in aquifers. Land use, and especially agricultural practices, controls nitrate concentration in springs, even though it does not determine its temporal variability. This claim is supported by the four different hydrological behaviors distinguished in this research, summarized as Hydrologic Response Types (HRT). They show different hydrological patterns, but nitrate remains constant over time.

EC and nitrate content in springs grouped in HRT1 are uniform over time. Water flows through a fracture system within crystalline rocks, which results in a uniform discharge of the spring all through the year with a constant low nitrate content due to the forestry land use. This is corroborated by the constant slope observed in the nitrate mass load curve, as well as by the variograms which show a progressive and continuous increment in the case of the discharge variograms, and a uniform variability or a pure nugget effect in the nitrate variograms. Springs in HRT2 show steady discharge, EC and nitrate concentration throughout the sampling period, as seen in the accumulated nitrate mass load. Such uniformity, with no influence from rainfall events, can be explained by the fact that these springs drain large, widespread surface deposits, and hydrochemical features can be homogenized within the aquifer.

In contrast, HRT3 springs respond to rainfall events. An increase in discharge and a decrease in EC are observed after rainfall, with the opposite trend being apparent after weeks of no rainfall. This suggests that mixing occurs between existing stored groundwater and recent infiltration within the same surface formation. Nitrate mass load curve is sensitive to rainfall events, mainly to that occurring in May. But small magnitude rainfall events that occurred in autumn and winter 2010 did not produce a response in the discharge, suggesting that some threshold infiltration rate is needed in these systems to trigger a change in their hydrological behavior. This effect of rainfall on discharge can be also observed in the variograms, which present higher range values than those of HRT1 and HRT2. Existing aquifer nitrate concentrations are as high as or even higher than (as in MDV003) those of recent infiltrating recharge that lixiviates the latest manure applications. Nitrate variograms depict such similarity of nitrate content, even in those springs where a slight increase (MDV003) or decrease (SJV003) in concentration generated a non-stationary time series that needed detrending.

Discharge and EC in the springs in the last group, HRT4, behave in a similar way and they are highly sensitive to rainfall. They both increased after rainfall, and decreased when no rainfall was recorded. The effect of rainfall, which causes changes in discharge, is seen in the nitrate mass curve. Nitrate also varies over time, usually in agreement with discharge variations. Nitrate changes however are smaller than those of discharge or EC. This might be the effect of a dual-flow system with contributions from surface deposits and underlying rocks, each with distinct recharge areas. The exception within this group is CAL004, which is influenced by stream water. In its case, groundwater contribution is important after rainfall, while stream water predominates after a dry period. For this reason, CAL004 reached 50% of total mass load early in May. The hole-effect in HRT4 discharge variograms points to how responsive each spring is to rainfall. The nitrate variograms do not present a common shape, reflecting the complexity of the specific conditions.

The accumulated mass load of nitrate, whether outflowing to streams or potentially recharging aquifers, indicates a roughly uniform build-up of the nitrate mass. However, those springs associated with recharge areas with a large storage capacity due to the size of the surface formations found in their recharge area, like HRT3 springs, and those where there is flow through the surface formations as well as through the underlying materials, like HRT4 springs, may show different patterns in the discharge rate of their nitrate mass load. They generally depend on major rainfall events and the hydrological response of the spring recharge area.

In summary, the times series analysis of discharge, EC and nitrate values distinguishes between different behaviors based on land use, geological setting and the response to the rainfall regime of each spring. Nevertheless, in almost all the springs studied, nitrate concentration is uniform over time with low variability. This shows the influence over the years of continuous fertilization, which matches the existing nitrate concentration of the aquifer resources with those of later infiltration events, independent of the hydrological processes that take place within the recharge area of the spring. Therefore, a homogenization of the nitrate content occurs in the subsurface that translates into the uniform nitrate concentration recorded in the surveys. It is patent that spring nitrate content reflects the land use type in the recharge area. However, manure application periods do not lead to a specific peak in nitrate records. Such stationarity has been shown in the variograms as large ranges or, in some specific cases, by a microvariability given by small ranges (almost a pure nugget effect) and small sills.

However, nitrate evolution shows indeed small variability in specific springs. For instance, TOR001, from HRT2; CAL005, and in a lesser degree MDV003, from HRT3; and these from HRT4 (CAL004, GUR004, SHV002 and SVT002) present variable nitrate concentrations usually around a mean value (Figures 3.4 to 3.7); except CAL004. Some of the major changes in nitrate concentration appear related to the rainfall regime, yet it does not result in abrupt nitrate variations (excluding CAL004 which, given its relationship with the nearby creek, presents an unusual behavior). Natural variability accounts for the magnitude of these temporal fluctuations as no major irrigation areas or large farms are found in the vicinity of the sampled springs.

Human pressures on nitrate concentration, however, were reported in deep wells as a mixing between the contribution of high-nitrate unconfined aquifers and low-nitrate leaky aquifers (Menció et al., 2011a). Nitrate evolution in those wells showed sudden large (> 50 mg/L) variations of nitrate content as the consequence of pumping on a complex multilayer aquifer system. Neither the hydrogeological setup of the springs nor their nitrate variability bears a resemblance to those corresponding in the monitored wells. Therefore, spring hydrology in areas with widespread nitrate pollution in groundwater shows we can expect a uniform nitrate concentration affected by natural fluctuations and subsequently, of the infiltrating water towards the unconfined aquifers. It is unrelated to the hydrogeological context that determines the occurrence of the spring. This conclusion can be drawn from the distinct geological scenarios with different recharge area sizes that were considered in this study. Flow lines that recharge groundwater resources at depth, instead of outcropping to the surface through springs, might then follow a similar behavior. We can thus expect a constant nitrate concentration in shallow aquifers after years of fertilization practices where flow fields have not been largely disturbed by groundwater withdrawal.

3.6 – CONCLUSIONS

Water from 13 natural springs in the Osona region was monitored every two weeks for a year to record their discharge, hydrochemical, and specifically nitrate content outflows. Underlying the study was the hypothesis that these springs reflect the infiltration flow towards the aquifer that ultimately determines nitrate content in groundwater and, therefore, its final quality for human uses.

In a region of such intensive agriculture, where fertilization using pig manure has been practiced for decades, nitrate content in wells and springs is usually above 50 mg/L. The selected springs lay in different geological settings under agricultural, forested or urban land uses. In all cases, the range of nitrate concentration was in line with the predominant land use of the spring recharge area. However, discrete events are observed in specific springs (HRT3 and HRT4), corresponding to large rainfall events, where loading rates are higher.

Geological setting and rainfall events control the discharge and hydrochemical characteristics of the subsurface flow as spring outflow and groundwater recharge. Four different types of hydrological responses (HRT) are identified in the area based on geology, discharge regime, electrical conductivity and nitrate content variations. In particular, discharge and electrical conductivity show a consistent behavior that determines the specific hydrogeological dynamics for each HRT. However, nitrate records generally appear uniform over time. Geostatistical analyzes also support the finding that nitrate content in most of the springs is uniform with small variability ranges. Some variograms reflect a hole-effect, indicating the impact of major rainfall events on nitrate outflow. Moreover, most accumulated normalized-nitrate mass load plots show a progressive increase in most springs over the 27 campaigns. Such a constant increment is evidence of a uniform subsurface nitrate mass flow towards the springs, and therefore to groundwater recharge.

From a management perspective, these findings have a twofold significance. First, the transfer of nitrate mass to streams, and its subsequent effect on stream ecology, can be assumed steady through the year, even though dilution processes depending on upstream discharge will determine its ecohydrological impact. Next, and from a hydrogeological perspective, unconfined aquifer recharge in agricultural areas shows a uniform nitrate occurrence in groundwater. The findings of this research suggest that land uses and agricultural practices, especially the amount of fertilizer applied over several decades, finally determines the magnitude of nitrate content in groundwater, although its variability remains small. Ultimately, geochemical processes in the subsurface, such as mixing and/or denitrification, as reported in Osona by Menció et al. (2011a) and Otero et al. (2009), will alter the amount of nitrate stored at depth and modify the infiltrating nitrate content, yet their effect appears to be steady over time.

In areas affected by diffuse pollution, monitoring of springs reveals a spatial variability of nitrate content and a temporal uniformity of its occurrence in shallow subsurface flows. Spring hydrological analysis thus stands as an indicator of groundwater recharge quality. On this assumption, significant major temporal fluctuations in nitrate content in aquifers could be attributed to flow regime alterations due to human pressures, principally groundwater withdrawal. In this sense, groundwater exploitation will induce undesired mixing from distinct hydrogeological layers with a negative effect on those of better quality. Appropriate borehole construction and pumping regimes should then be utilized to preserve those aquifers with low nitrate pollution and to reduce the risk of spreading nitrate to non-(or less) polluted aquifer layers.

CHAPTER 4

Regression model for aquifer vulnerability assessment of nitrate pollution in Osona (NE Spain)

The contents of this chapter are an edited version of the manuscript submitted to *Journal of Hydrology* in June 2013 to be considered for publication by M. Boy-Roura, B.T. Nolan, A. Menció and J. Mas-Pla.

4.1– INTRODUCTION

Water pollution is a major concern in water management in most of the world's 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 Europe, the Nitrate Directive 91/676/EC (EC, 1991), Water Framework Directive 2000/60/EC (EC, 2000) and Groundwater Directive 2006/118/EC (EC, 2006) consider nitrate contamination as one of the main threats to groundwater quality, requiring urgent and intensive monitoring and a strong policy. For instance, the Nitrate Directive aims to protect water quality by preventing nitrates from agricultural sources polluting water bodies and by promoting the use of good farming practices. Therefore, member states are asked to designate Nitrate Vulnerable Zones (NVZs). Elevated concentrations of nitrate in drinking water are also a human health concern. Recent studies show that the ingestion of nitrate even below the WHO guideline of 50 mg/L of nitrate (WHO, 2008) in drinking water has been associated with increased risk of certain cancers, adverse pregnancy outcomes, diabetes and thyroid disorders (Ward et al., 2005; Ward and Brender, 2011).

Determining where groundwater may be more vulnerable to contamination can help water managers prioritize areas for monitoring and implementation of alternative agricultural management practices. The vulnerability of groundwater is a function of the properties of the aquifer system that govern groundwater flux and the fate and migration of pollutants (intrinsic susceptibility), as well as the location and characteristics of contaminants sources, either naturally occurring or anthropogenic (Focazio et al., 2002). Vulnerability assessment is based in the susceptibility of a particular aquifer to contaminant sources that could affect groundwater quality (e.g. nitrates, industrial chemicals, gasoline). This type of assessment often results in a map of areas where the resource is vulnerable to contamination from surface activities (Liggett and Talwar, 2009). Groundwater vulnerability assessment is also a powerful educational tool for raising public awareness of water resources protection issues, which is an on-going need (Nowlan, 2005).

In general, there are three categories of models for assessing groundwater vulnerability: index methods, statistical methods and process methods. On the one hand, index methods assign numerical scores or rating directly to various physical attributes to develop a range of vulnerability categories. The most widely used index method is DRASTIC (Aller et al., 1985). However, assignment of weights in DRASTIC is subjective and is not informed by the data. On the other hand, statistical methods range from simple summary and descriptive statistics of concentrations of targeted contaminants to more complex regression analyses that include the effects of several predictor variables. When a dataset of water quality and potential explanatory variables is available, statistical models in the form of regression equations can be used to predict probabilities or concentrations of contaminants and are typically used in places with diffuse sources of contamination, such as to detect nitrate patterns over agricultural areas. In particular, logistic regression is a statistical method that predicts a probability of occurrence (Helsel and Hirsch, 1992). Statistical models account for the influence of explanatory variables through model coefficients which are estimated during model calibration. Finally, process-based methods refer to approaches that either simulate or otherwise take into account physical processes of water movement and the associated fate and transport of contaminant in the environment. A well-known example is MODFLOW (i.e., Harbaugh et al., 2000), with its associated packages and codes that solve the governing equations of groundwater flow and solute transport. Such models have explicit time steps and are often used to determine the time scales of contaminant transport to wells and streams, in addition to the effects of pumping. However, they also have many parameters that require estimation.

Empirical models typically have fewer parameters and have been successfully applied to predict the concentration or the likelihood of contamination of groundwater by various chemicals at large spatial scales. In the United States, the U.S. Geological Survey (USGS) has performed different studies regarding groundwater susceptibility and vulnerability in relation to various explanatory factors and were carried at different spatial scales. Many investigators used logistic regression analysis (LR) in order to predict the probability of nitrate concentrations in groundwater exceeding a certain threshold. For instance, LR was used by Tesoriero and Voss (1997) to evaluate aquifer susceptibility and groundwater vulnerability in the Puget Sound Basin. Nolan (2001) and Nolan et al. (2002) applied a logistic regression model to identify variables to predict the probability of exceeding 4 mg/L of nitrate in shallow, recently recharged groundwater of the United States. Nitrate contamination at multiple thresholds was evaluated in the Mid-Atlantic Region in the USA using LR (Greene et al., 2005). LR has been also used to predict the probability of other contaminants. For example, Rupert (2003) used this technique to predict the probability of detecting atrazine/DEA in groundwater in Colorado, and Lindsey et al. (2006) used LR to study the presence of nitrate, pesticides, VOCs and radon in the Piedmont Aquifer System (Eastern United States). Although the above models have performed well with groundwater contaminant data, LR yields probabilities rather than concentrations. Concentrations are often preferred because they can be directly compared with drinking water standards and health advisories. Multiple linear regression (MLR) predicts concentrations and is conceptually similar to logistic regression because relations between one dependent variable and several independent variables are evaluated (Kleinbaum, 1994). MLR was used to describe the relationship of nine variables to observations of triazine concentrations in groundwater in Nebraska (Chen and Druliner, 1988). Steichen et al. (1988) also used MLR to relate pesticide concentrations in groundwater to the age of the well, land use around the well, and distance to the closest possible source of pesticide contamination. Stackelberg et al. (2006) used MLR and Tobit regression models (Stackelberg et al., 2012) to predict atrazine frequency for shallow groundwater of the United States. Nonlinear MLR models were also developed to predict contamination of shallow groundwater by nitrate and also in deeper drinking-water wells (Nolan and Hitt, 2006).

Most of the studies have commonly been conducted at national and regional levels, and logistic regression was an effective method despite the extreme spatial variability of groundwater quality and related factors. However, due to the same source of nitrogen, the widespread nitrate pollution in the Osona region and the interest to predict nitrate concentrations rather than probabilities, multiple linear regression was chosen over logistic regression. To accommodate the complexity of the hydrogeological system, vertical aquifer heterogeneities were addressed in the modeling. Therefore, the objectives of this study are: 1) to determine which variables are relevant to simulate nitrate concentration in groundwater, including the differentiation between unconfined, leaky and confined aquifers, using MLR; 2) to predict nitrate concentrations at a sub-regional scale; and 3) to create a vulnerability map of the Osona region to assess which areas need enhanced monitoring and protection for water resources.

4.2 – THE STUDY AREA

The Osona region is located in Catalonia, in the NE of Spain. It has an area of 1,260 km2 and a total population of 153,500 inhabitants. This is an intensive agricultural and livestock production area. In 2010, there were 822 hog Animal Feeding Operations (AFOs) and more than 860,000 head of livestock (hogs and cattle). In 2009, a total of 38 out of 51 municipalities in Osona, which represents 70% of its area and the totality of its agricultural land, were declared as vulnerable to nitrate pollution from agricultural sources by the Catalan Parliament (Decret 136/2009). Because of these reasons, this study considers the whole Osona region defined by its administrative boundaries over natural or hydrogeological limits. The 90.6% of the manure generated by livestock production is spread as fertilizer on the crops and most of them are situated in Plana de Vic, the flat central part of the study area where most of the agricultural activity occurs. The most common crop is wheat (30%), followed by barley (20%), corn (14%) and sorghum (5%), among other minor crops. About 98% of the total cultivated land (23,906 ha / 239.06 km2) are non-irrigated crops. Only 9.4% of the manure produced is treated in treatment plants.

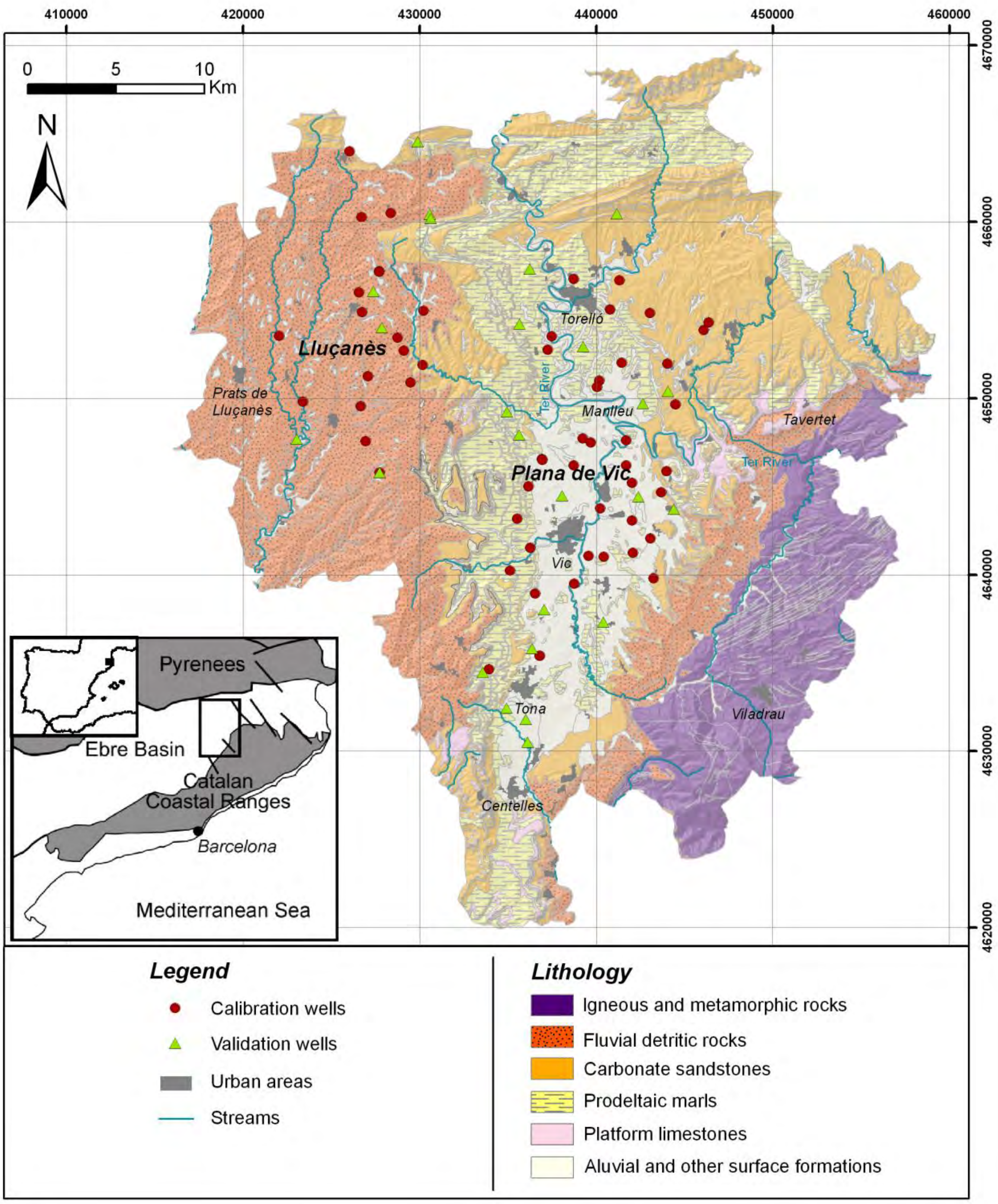


***Figure 4.1** – Geological map and geographical situation of the study area, with the locations of the wells. Geological formations are mapped according to the main lithology in the area (geological cartography simplified from IGME, 2006).*

Nitrate concentrations in groundwater are commonly above 50 mg/L, reaching up to 500 mg NO3/L in some of the sampled wells. Menció et al. (2011b) and Otero et al. (2009) studied the pollution sources and the distribution of nitrate in groundwater in the Osona region from local and regional hydrogeological perspectives. Vitòria (2004) used δ15NNO3 and δ18ONO3 to confirm the link between groundwater nitrate pollution and pig manure. Furthermore, Otero et al. (2009), Torrentó et al. (2011) and Vitòria et al. (2008) used environmental isotopes to report the occurrence of natural attenuation processes (denitrification) in this region. Logistic regression and ANOVA analysis identified the importance of land use and geological setting in nitrate pollution in springs in Osona (Menció et al., 2011a). These analyses showed that nitrate pollution was more dependent on land use than on the geological setting of springs. Boy-Roura et al. (2013) concluded after a survey of 13 springs in the Osona region during a year that nitrate concentrations in unconfined aquifer units remained steady over time with only minor influence from external factors, such as rainfall events and fertilization regimes.

The study area has a sub-Mediterranean climate with hot summers and cool winters. The annual mean temperature is 12.6 °C, mean precipitation and potential evapotranspiration are around 715 and 706 mm/year, respectively. Spring and autumn are the rainiest seasons. In summer, potential evapotranspiration is usually twice as much precipitation.

The geological system of the Osona region consists of a sequence of Paleogene sedimentary layers, with a total thickness of approximately 1,500 m, which overlies the Hercynian crystalline rock (igneous and metamorphic) basement. The stratigraphic sequence consists of a thick (≈500 m) basal level of conglomerates at the bottom, and a succession of carbonate formations with alternating calcareous, marl and carbonate sandstone layers (Figure 4.1; see stratigraphic column and geologic cross-section in Otero et al., 2009; Menció et al., 2011b). These formations show a dipping to the west of about 5-10° that is quite uniform, and only have an antiform structure at the northern border of the study area (the Bellmunt anticline). Nevertheless, significant variation in thickness and facies transitions are common in this sedimentary basin, as evidenced by signs of a strong structural influence in its evolution during the early Tertiary. Despite this structural control during the Palaeogene, faults were not significant later on, and especially not during the Quaternary. Therefore, the present morphological features of the Plana de Vic basin are not defined by major structural elements, but are related to erosion processes controlled by the evolution of the River Ter drainage basin, or the groundwater flow.

From a hydrogeological prospective, those carbonate formations constitute a multi-layered aquifer system. Aquifers located in carbonate and carbonate-sandstone layers have a porosity related to the fracture network of variable density, roughly oriented N-S and E-W throughout the study area, and occasionally is due to dissolution. Fractures may eventually affect marls in specific areas, when their sand content is significant, and consequently act as aquitards, permitting a vertical leakage to the underlying leaky aquifers. Occasionally, marl layers may act as aquicludes, and therefore they act as truly confining layers. Therefore, confined aquifers can also be found in the study area.

In the central part of the region, quaternary sediments overlay the sedimentary formations and support agricultural activity. In particular, the main alluvial formations are located in the central part of the basin and constitute local unconfined aquifers, especially in the Ter River terraces and its floodplain. Other quaternary formations, such as colluvial, eluvial, and mass-wasting deposits, also form potential small-scale hydrogeologic units. Shallow wells (<30 meters deep) are located in the alluvial aquifers, while deeper wells usually reach 100 m or even deeper in search of the more productive aquifers.

4.3– METHODOLOGY

4.3.1 – Calibration data set

The calibration data set consisted of 57 private wells sampled in May 2010. These wells are mainly used for farm supply and in few cases, domestic supply; none of them are used for irrigation purposes. Physical-chemical parameters (pH and electrical conductivity) were determined in the field and a full ion analysis of water was performed using standard methods. Isotope data ($\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, $\delta^{34}S$, $\delta^{18}O_{SO4}$, $\delta^{13}C_{HCO3}$, $\delta^{18}O$ and δD) of the same wells belonged to two sampling campaigns done in 2005 in Plana de Vic (central part of the study area) and 2008 in Lluçanès (western part; Mas-Pla et al., 2006; Mas-Pla et al., 2008; Otero et al., 2009). We assume that isotope data from previous sampling campaigns are valid to use in the MLR together with data from 2010. The isotope data add significant information about geochemistry processes in groundwater. Groundwater ages based on tritium data were used to qualitatively determine the water residence time in the aquifer, for comparison with the timeframe of land use and fertilization loadings. Tritium data from precipitation samples from the Barcelona station were used and complemented with other western Mediterranean stations (Marseille, Avignon and Gerona Airport) to complete the series between 1961-2007 (IAEA and WMO, 2006).

The validation procedure consists of 25 wells sampled in 2005 and 2008 (Menció et al., 2011b).

4.3.2 – Explanatory variables

Characteristics of nitrogen sources and aquifer susceptibility to contamination were evaluated by developing a set of explanatory variables for use in the MLR model. Up to 70 explanatory variables, which are summarized in Table 4.1, were screened in MLR using stepwise best subsets analysis in SAS® software. Stepwise procedures are automated model selection methods in which the computer algorithm determines which model is preferred. Best subsets routine compares all models having the same number of explanatory variables and ranks them by R^2. Moreover, other possible models where evaluated introducing, manually, variables of interest that could explain aquifer vulnerability. In this manner, all possible models could be screened. Taking into account all these steps and criteria, the final model with better performance was selected. Variables were checked for statistical significance using p-values for the t-test.

Some variables, such as N loading and % of land use (see Table 4.1), were compiled within 500-meter radius buffers around the wells, which are an effective surrogate for the contributing areas of the wells (Johnson and Belitz, 2009). Data within the well buffers were extracted using a GIS-based weighted average method called NACT tool (Price et al., 2010). This toolbox is composed of a collection of custom tools that implement geographic information systems (GIS) techniques used by the NAWQA Program to characterize aquifer areas, drainage basins, and sampled wells. In this study, the aim for using this tool was to process area weight data values associated with the source (e.g.: assigning total manure load to agricultural areas within a municipality) to the target area of interest (e.g.: agricultural areas within the well buffers).

Other variables such as soil and geological characteristics were compiled as point data because their GIS polygons were larger than well buffers and values were the same within this area.

Most of the variables were continuous, but in some cases, they were categorical (i.e., aquifer type and hydraulic conductivity). Categorical variables were treated as ordinal variables so they could be used quantitatively in the MLR model. First, these variables were classified and ordered into different categories and then, a score was assigned to each category.

A simple innovative nitrogen mass balance was implemented for the purpose of calculating net nitrogen load to groundwater. Nitrogen loading from animal manure was compiled at the municipality level from 2010 animal population data, based on the stage nitrogen-production rates for hogs and cattle. The amount of manure processed in treatment plants was subtracted from the manure loading to reflect the net manure nitrogen load that was produced at each municipality. Municipality-level net manure loading was apportioned in a GIS by agricultural land using the NACT tool to reflect variations in loadings within municipalities and to achieve greater spatial accuracy. We assumed that all manure produced is applied to agricultural land within the same municipality. However, it is known that in three municipalities in the northern part of Osona, manure is transported to the Ripollès region, in the north of the study area, where there is a larger agricultural area available for fertilization and road transport is faster. Unfortunately, these data were not available and therefore, nitrogen loading variable could not be calculated for these areas and it is shown as "no data" in the nitrogen load map and vulnerability maps. Commercial chemical fertilizers were not accounted for as a potential variable for nitrogen sources as its use is almost negligible due to the large amount of organic fertilizer produced in the area (Otero et al. 2009; Vitòria, 2004). Crop nitrogen uptake was considered as an estimate of nitrogen outputs. It was calculated at the municipality level by taking into account the nitrogen that each crop type extracts (kg N/1000 kg) times the crop yield (kg/ha) for irrigated and non-irrigated crops. Nitrogen uptake by crops was also apportioned by agricultural land, and nitrogen uptake was subtracted from net manure nitrogen load to represent the potential nitrogen input to groundwater. The above steps reflect mass balance considerations for nitrogen applied in the Osona region.

Regarding aquifer susceptibility variables, a binary variable was created to indicate presence or absence of different lithologies; for instance, presence of alluvial sediments was coded 1, and 0, if they were absent. Shallow wells located in coarse-grained surficial deposits are the most susceptible to elevated nitrate concentrations because they tend to receive water with show flow paths, and these parts of the aquifer are more likely to have oxic water, enhancing nitrate mobility. In contrast, wells with fined-grained surficial deposits are representative of longer flow paths and are more likely to have waters which favor nitrate reduction. The same procedure was done concerning soil characteristics variables. Soil drainage characteristics influences nitrate concentration in shallow groundwater. Well-drained soils generally are coarse-grained and can easily percolate water and nitrate to groundwater. In contrast, poorly drained soils commonly are fine-grained and transmit water and nitrate at a slower rate than

	Model parameter	Units	Variable type	GIS compilation area	Data source	Comments
NITROGEN SOURCES	**Net N load**	kg/ha	Continuous	500m well buffer	Livestock census 2010; DAAM, SIR (2011a)	Manure produced minus manure treated.
	Crop N uptake	kg/ha	Continuous	500m well buffer	Crop production data; DAAM, SIGPAC(2011b)	Representing N outputs.
	Potential N input to groundwater	kg/ha	Continuous	500m well buffer	Own data	N budget (N load minus crop N uptake).
	% agricultural land	%	Continuous	500m well buffer	1:5,000 land cover map; CREAF (2011)	Representing N pollution from agricultural sources.
	% urban land	%	Continuous	500m well buffer	1:5,000 land cover map; CREAF (2011)	Representing N pollution from urban sources.
	% forested land	%	Continuous	500m well buffer	1:5,000 land cover map; CREAF (2011)	Representing absence of N inputs.
	Population density	inhab/km^2	Continuous	500m well buffer	IDESCAT (2012)	Representing N pollution from urban sources.
AQUIFER SUSCEPTIBILITY	Climate data	mm, ºC	Continuous	Point data	SMC (2012)	Representing the potential recharge. Monthly rainfall, ETP and temperature data from 4 weather stations in the study area (1940-2000).
	Geology type (8 variables)	0/1	Binary	Point data	1:50,000 geological map; IGME (2006)	Distinguishing among different lithologies: coarse alluvium sediments, fine alluvium sediments, marls, sandstones, conglomerates, micro conglomerates, siltstones, and shales.
	Aquifer type	[-]	Categorical	Point data	Own data	Distinguishing among unconfined, leaky, and confined aquifers.
	Well depth	meters	Continuous	Point data	Own data	Depth of the well.
	Soil type (10 variables)	%	Continuous	Point data	1:250,000 soil map; IGC (unpublished data)	Distinguishing among Haplic Leptosol, Haplic Regosol, Haplic Cambisol, Haplic Fluvisol, Haplic Calcisol, Haplic Luvisol, Rendzic Leptosol, Petric Calcisol, Cambic Leptosol, and outcrops.
	Soil characteristics (9 variables)	0/1	Binary	Point data	1:250,000 soil map; IGC (unpublished data)	Soil depth, texture (4 classes), abundance of coarse sediments (3 classes), and drainage.
	Hydraulic conductivity	m/day	Categorical	Point data	Literature; Freeze & Cherry, 1979	Values taken from literature according to aquifer dominant lithologies.
	Slope	%	Continuous	Point data	SIGPAC-DAAM (2011b)	Representing runoff as a recharge controlling factor.
FATE	**Irrigated crops**	%	Continuous	500m well buffer	Agricultural plot identification system; SIGPAC-DAAM (2011b)	Percent of irrigated crops within the well buffer.
	Chemistry (27 variables)	several units	Continuous	Point data	Own data, Menció et al. (2011b) & Otero et al. (2009)	Major ions, physical-chemical parameters and isotope data.
	PCA factors (3 variables)	[-]	Continuous	Point data	Own data	First 3 PCA factors.

Table 4.1 – *Explanatory variables screened in the MLR analysis; in bold, the ones included in the model.*

well-drained soils. Poorly drained soils also are anaerobic, which promotes conversion of nitrate to nitrogen gas and limits conversion of ammonia to nitrate.

Climate data was checked to be included as a variable in the model, as it indicates the potential for groundwater recharge that influences nitrate transport through the unsaturated zone.

A second innovation involved generating an ordinal variable to classify wells according to which aquifer type they belonged to, based on prior hydrogeological analysis of the recharge setting (Menció et al., 2011b), hydrochemical data and, where available, isotope data. In this way, the model addresses vertical aquifer heterogeneity. A score of 1 was given to wells located in unconfined aquifers, 2 for those in leaky aquifers and 3 for wells in confined aquifers. In few cases, mid-point values were given to wells that could not be clearly classified in one aquifer type (e.g., 1.5 for unconfined/leaky aquifers, and 2.5 for leaky/confined aquifers). Because aquifer type was a point data variable, specific values are needed to be assigned when running the MLR model.

A third innovation used Principal Component Analysis (PCA) of groundwater chemistry, isotope data and physical-chemical parameters to identify hydrological processes and if relevant, to create a composite, mappable variable for inclusion in the MLR model. PCA factors that explained above 50% of the variability in groundwater chemistry (higher eigenvalues) were tested to be included in the model as explanatory variables. Selected PCA scores for each well were interpolated by kriging, based on a previous variogram analysis, to obtain a map of this variable.

All the variables in the model were finally recompiled within a 10 meters grid cells using GIS to predict the nitrate concentration in the Osona region.

4.3.3 - Model development and vulnerability maps

Multiple linear regression (MLR) was used to predict nitrate concentration in groundwater. The goal of MLR is to explain as much as possible of the variation observed in the response variable (*y*), leaving as little variation as possible to unexplained “noise” (Helsel and Hirsch, 1992). MLR model is denoted as:

$$y_i = \beta_0 + \sum_{j=1}^{n} \beta_j x_{i,j} + \varepsilon_i, \qquad i = 1, m \qquad (1)$$

where y_i is the response variable at location *i*, β_0 is the intercept, β_j are the slope coefficients of the explanatory variables $x_{i,j}$, *n* the number of variables, and *m* is the number of locations or wells. ε_i is the remaining unexplained noise in the data (the model error or regression residual). The response variable, that is nitrate concentration in groundwater, was natural log transformed (ln) to stabilize the variance. The coefficients were calculated using ordinary-least-squares (OLS) regression, which weight the influence of the explanatory variables.

Model performance was evaluated for several MLR models with a combination of distinct significant explanatory variables. Model fit and diagnostics were checked to select the model that performed better and had a consistent conceptual hydrogeological meaning. Model fit statistics were based on the significance level of estimated coefficients (p-values for the t-test), the coefficient of determination (R^2), the root mean squared error (RMSE), the prediction error sum of squares (PRESS) and Akaike's information criteria (AIK). Cook's D was used as a regression diagnostic to identify unusual predicted values with high leverage. High values of R^2 and low values of RMSE, PRESS and AIK indicate a better performance of the model. Tolerance was also assessed to examine if multicollinearity existed between variables. As a rule of thumb, if tolerance is less than 0.20, a problem with multicollinearity is indicated (Menard, 2001). Plots of model residuals and plots of predicted versus observed values were used as visual evidence of goodness of the fit. In model validation, predicted and observed values were plotted and visually compared with a 1:1 line to check model fit and bias.

After the coefficients were determined through regression analysis and model performance was evaluated, the Eq. (1) was transformed back to its original units to estimate nitrate concentrations in mg/L in the Osona region and to create vulnerability maps. Duan's (1983) smearing estimate was selected as an appropriate bias correction factor (BCF) to correct the bias present in the retransformed logarithmic equation that was created using OLS regression.

The retransformed equation has the following form:

$$y_{i,D} = BCF_D \cdot exp^{\left[\beta_0 + \sum_{j=1}^{n} \beta_j x_{i,j} + \varepsilon_i\right]} \qquad (2)$$

$$BCF_D = \frac{\sum_{i=1}^{m} exp^{\varepsilon_i}}{m} \qquad (3)$$

where $y_{i,D}$ is the dimensional smearing estimate at location *i*, and BCF_D indicates the Duan's bias correction factor.

4.4– RESULTS AND DISCUSSION

4.4.1 – Calibration data set

Observed nitrate concentrations for the calibration wells ranged between 2.2 mg/L to 590 mg/L. All nitrate concentrations are reported as nitrate. About 70% of the wells had nitrate content above 50 mg/L, which is the threshold for drinking water (Figure 4.2a). Tritium data measured at 20 wells ranged between 2.7 to 6 TU. A lumped parameter age distribution model (piston-flow) using tritium data indicated that all water samples infiltrated after 1980 till present. Therefore, water samples are representative of the period when intensive livestock activities started in the Osona region, in the late 1980's.

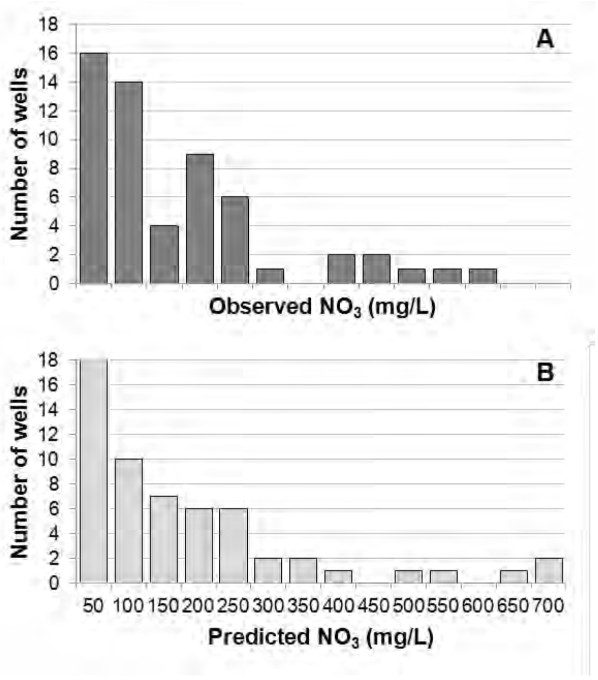


Figure 4.2 – *Frequency distribution (histograms) of the observed (A) and predicted (B) nitrate concentrations of the 57 wells used in the calibration of the MLR model.*

4.4.2 – Examination of the explanatory variables through the calibration process

Explanatory variables with p-values lower than 0.10 were significant and were included in the MLR model. In some cases, however, two variables could be used to represent similar information because characteristics of some variables are implicit to other variables. For instance, concerning nitrogen sources variables, either percent of agricultural land and N loading could have been included in the model because both p-values were lower than 0.10 (Table 4.2). Finally, N load was selected because it performed better in the MLR with a lower p–value (0.0013), and it was better suited from a management point of view; that is, to predict how nitrate concentrations would change if different N manure loads were applied. Other variables classified as N sources (Table 4.1) were statistically not significant, and therefore not included in the model.

Parameters related to aquifer susceptibility can be divided into variables representing transport to aquifers and attenuation processes. Climate data play a role in transport of nitrate to groundwater. Wilcoxon test and t-test concluded that monthly average rainfall, temperature and evapotranspiration data were not significantly different among the distinct weather stations indicating a homogenous climate in all the study area. Therefore, they were not taken into account in the model. Aquifer type was the most significant variable in the model with the lowest p-value (<0.0001). This variable brings information about the hydrogeological system where the well is located and allows differentiating the vulnerability of the distinct aquifer types. Variables such as presence of different lithologies, hydraulic conductivity or well depth could be surrogates for aquifer type. Nevertheless, they were not statistically significant. Presence of coarse alluvial sediments was the only type of lithology significant in the model. The characteristics of these sediments allow the development of deep and well-drained soils, i.e., Haplic Calcisol. This type of soils was another statistically significant variable. Either occurrence of coarse alluvial sediments or presence of Haplic Calcisol soils could have been included in the MLR because they represented similar information. Finally, the later was added in the model because it had a lower p-value. Other soil types and characteristics had p-values higher than 0.10 and consequently were not included.

Percent of irrigated crops was also significant in the model and it was classified as an attenuation variable because irrigation using stream water was found to act as a dilution effect.

Groundwater chemistry, physical-chemical and isotope data were tested in the model, firstly, as single variables for each parameter. Some of them were significant in the model, but they could not explain any geochemical process neither were typically thought of as affecting nitrate, and did not add any relevant information in the model. For this reason, a PCA analysis was performed to reduce chemistry, isotope and physical-chemical data to composite a new variable that represents hydrochemical processes. Table 4.3 shows the three first factors of the PCA that explained the 52% of the variability of the data. These three factors were tested in the MLR analysis. However, only factor 3 was included in the final model because it was the most significant in the regression. The components with higher loads in factor 3 are dissolved O_2 (negative sign) and, HCO_3^-, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ (with a positive sign), which can be indicative of denitrification processes within the aquifer, and can be associated to the concept of natural attenuation. Denitrification processes were already reported in the Osona region in previous studies (Otero et al., 2009; Vitoria et al., 2008), where a multi-isotopic approach analyzing the ions involved in denitrification reactions showed a link between denitrification and pyrite oxidation. Denitrification requires anoxic conditions where NO_3 is reduced to N_2 or N_2O by organic matter or sulfide oxidation (Moncaster, 2000; Pauwels, 2000; Tesoriero et al., 2000). Denitrification by sulfide oxidation occurs in several steps:

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4Fe^{2+} + 8SO_4^{2-} + 8H^+ \quad (4)$$

$$10Fe^{2+} + NO_3^- + 14H_2O \rightarrow 10FeOOH + N_2 + 18H_2O \quad (5)$$

In aerobic media, sulfide oxidation can take place by the decrease of the dissolved O_2 in water (Eq. 4). The production of protons induces calcite dissolution and therefore, there is an increase in HCO_3^-. When Fe^{2+} produced is oxidized, a global reaction can be written.

$$6NO_3^- + 2FeS_2 + 2H_2O \rightarrow 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+ \quad (6)$$

The decrease in NO_3 concentration is coupled with an increase in the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ of residual NO_3 (Kendall, 1998). In the PCA analysis, each well gets its score for Factor 3, which is used to extrapolate the values to the whole study area using kriging.

4.4.3 – Model building

The final model includes the following five variables: 1) nitrogen loading, 2) aquifer type, 3) percent well-drained and deep soils, 4) percent irrigated crops, and 5) an indicator of the occurrence of denitrification processes (Figure 4.3). Parameter coefficients have positive or negative signs depending on whether they increase or decrease the predicted amount of nitrate in groundwater (Table 4.2).

The net nitrogen load variable that represents the kg/ha of manure nitrogen applied on agricultural land has a positive coefficient sign. As expected, nitrate concentration is higher in those areas where more manure is applied (Figure 4.3a). Aquifer type is another explanatory variable that is considered to most significantly influence nitrate concentration of groundwater (Figure 4.3b). Aquifer type has a negative estimated coefficient showing that higher nitrate concentrations are more likely to be found where the well is located in unconfined aquifers and unconfined/leaky aquifers (rated with a categorical value of 1 and 1.5, respectively) and lower concentrations in deeper, leaky, leaky/confined and confined formations (rated 2, 2.5

and 3, respectively). The categorical value given to each well, according to its aquifer type, corrects the estimation of the coefficient for the depth factor. This coefficient is thus valid for any aquifer type as it has been optimized in consonance with the actual nitrate concentration together with the other variables included in the MLR.

	Factor 1	**Factor 2**	**Factor 3**
EC	-0.89	-0.33	-0.19
Mg^{2+}	-0.83	-0.45	0.1
Na^{+}	-0.77	0.02	0.2
Cl^{-}	-0.76	0.16	-0.19
Ca^{2+}	-0.70	-0.42	-0.38
Br^{-}	-0.50	0.22	-0.05
$\delta^{18}O_{SO4}$	0.42	-0.78	0.05
SO_4^{2-}	-0.59	-0.66	0.02
$\delta\,^{34}S_{SO4}$	0.27	-0.65	-0.29
δ D	-0.45	0.54	-0.33
$\delta\ O^{18}$	-0.44	0.58	-0.35
O_2	-0.01	-0.05	**-0.75**
HCO_3^{-}	-0.28	-0.08	**0.54**
$\delta\,^{15}N_{NO3}$	-0.36	0.54	**0.57**
$\delta\,^{18}O_{NO3}$	-0.23	0.31	**0.75**
Fe^{2+}	0.16	-0.42	0.1
Si^{2+}	0.06	-0.28	-0.24
K^{+}	-0.28	0.03	0.07
pH	0.01	0.39	-0.28
Mn^{2+}	-0.33	-0.44	0.12
Ba^{2+}	0.33	0.34	-0.11
$\delta\,^{13}C_{HCO3}$	-0.16	0.32	-0.27
Eh	0.06	0.42	-0.42
Eigenvalue	5.01	4.04	**2.75**
Proportion explained variance	0.22	0.18	**0.12**

In bold, components explaining denitrification processes.

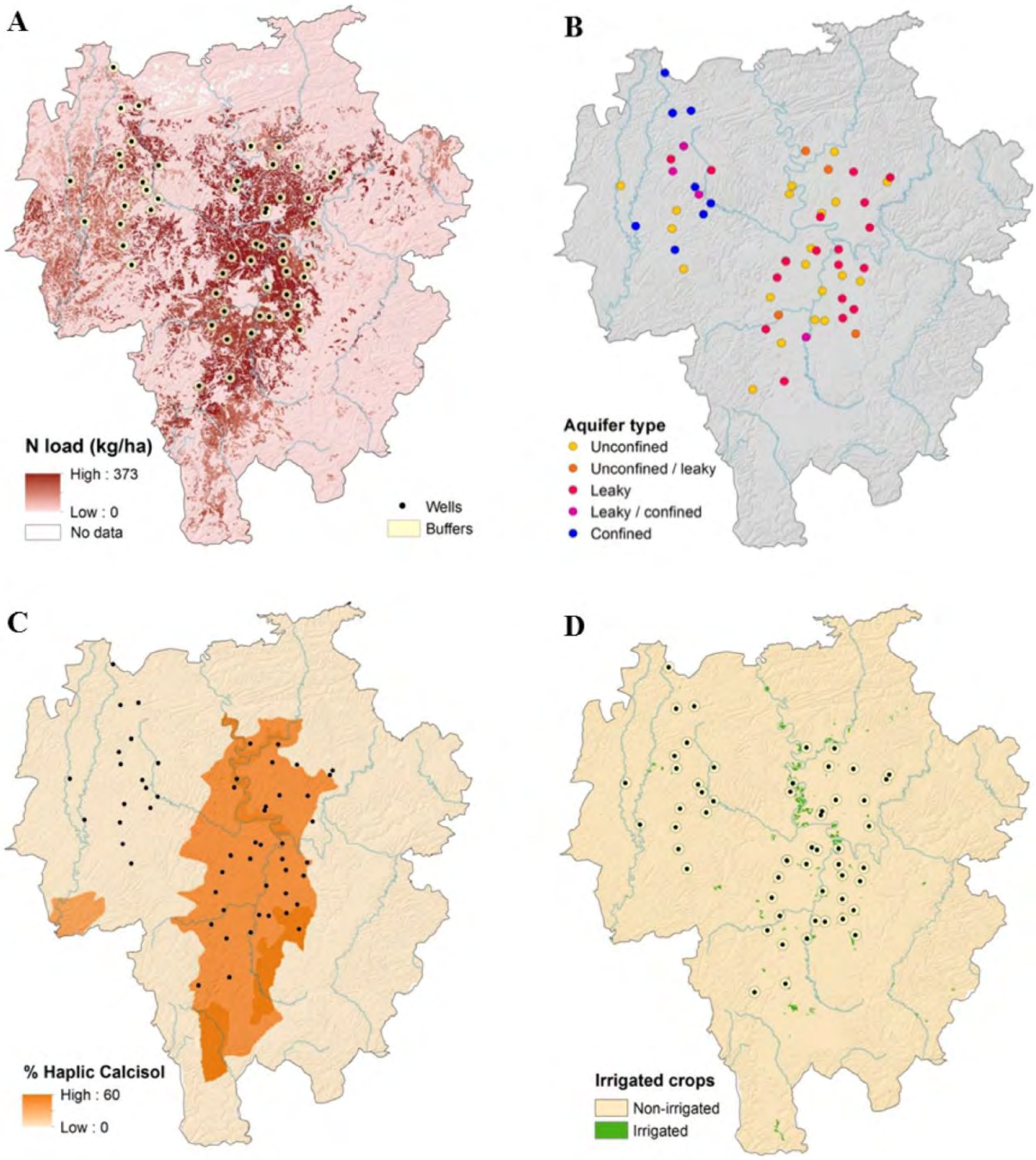
Table 4.2 – *PCA factor loadings for each variable.*

The third variable represents the percent of Haplic Calcisol soil type, which are deep, well-drained soils and permeable, which can readily leach water and nitrate to groundwater. Nitrate leaching in the central part of the study area is enhanced due to the occurrence of this soil type. These soils are also productive and suitable for agricultural activities (Figure 4.3c). Hence, nitrate applied on the crops can be transported with ease to groundwater and a higher risk of water contamination is thus expected. The fourth variable included in the MLR model stands for the percent of irrigated crops in the well buffer (Figure 4.3d). Most of the irrigated crops are located near streams, and therefore surface water with low nitrate concentrations (<15 mg/L; ACA, 2012) is used to water them. The negative coefficient indicates that the occurrence of irrigated crops acts as dilution effect. The last variable included in the model is an indicator of the presence of denitrification processes. High values of this factor indicate that denitrification processes are occurring, while lower values show absence of denitrification (Figure 4.3e).

Variable (β_j)	**Estimated coefficient**	**p -value**
Constant (β_0)	4.67884	<0.0001
Net nitrogen load (kg/ha)	0.00529	0.0013
Aquifer type	-0.73102	<0.0001
Haplic Calcisol soil type (%)	0.02024	0.0612
Irrigated crops (%)	-0.03788	0.0858
Denitrification	-0.24440	0.0148

Table 4.3 *– Explanatory variables in the final multiple linear regression model.*

The MLR model using these five variables yielded an R^2 of 0.75, indicating that 75% of the variation in nitrate concentration in the Osona region is explained by the model. A histogram of the predicted nitrate concentrations is presented in Figure 4.2b and model parameters (p-values) are shown in Table 4.2. Model residuals are normally distributed (Figure 4.4). In the normal probability plot, it is shown that most of the residuals fall along the normal distribution line indicating a satisfactory goodness of fit for all aquifer types. Nonetheless, two outliers in the lower left corner of this graph correspond to confined aquifers with very low nitrate concentration. A plot of observed versus predicted log nitrate (ln NO_3) concentrations indicates that the MLR model successfully fits the observed data (Figure 4.5a). This figure also reveals that the same outliers from confined aquifers above mentioned present over predicted concentrations. Despite these wells had higher Cook's D values compared to the rest of the wells (but lower than the critical value), they were kept in the MLR to represent the whole range of nitrate concentration values in the area. A plot of the residuals of log nitrate versus the predicted log values shows that variance of the residuals is constant, which satisfies the regression assumption of homoscedasticity (Figure 4.5b). Tolerance was higher than 0.2 in all variables, indicating there were no problems of multicollinearity.



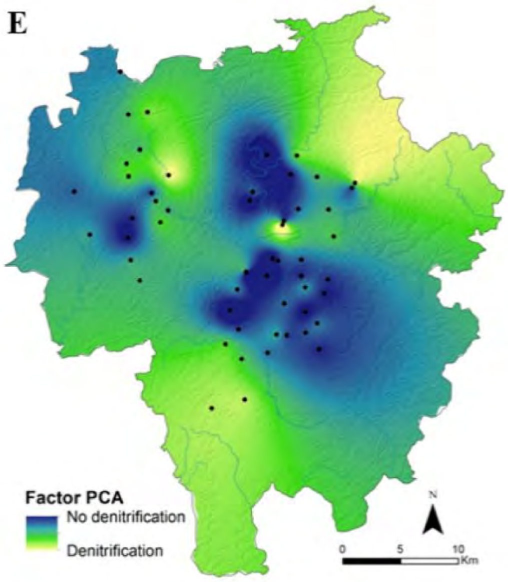


Figure 4.3 – *Spatial distribution of the explanatory variables included in the MLR model: nitrogen load (A), aquifer type (B), percent of well-drained and deep soils (Haplic Calcisols) (C), percent of irrigated crops (D) and factor 3 of the PCA showing presence or absence of denitrification processes (E). No data refers to missing values of nitrogen load variable for these areas (see section 3.2).*

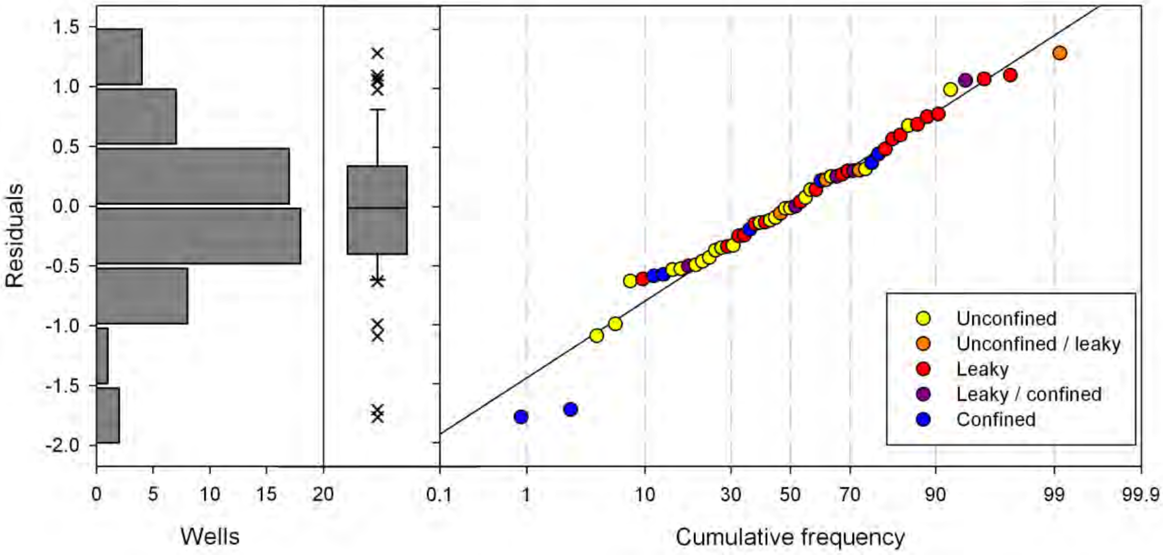


Figure 4.4 – Histogram (left side), boxplot with outliers (middle), and normal probability plot (right) of the distribution of the residuals.

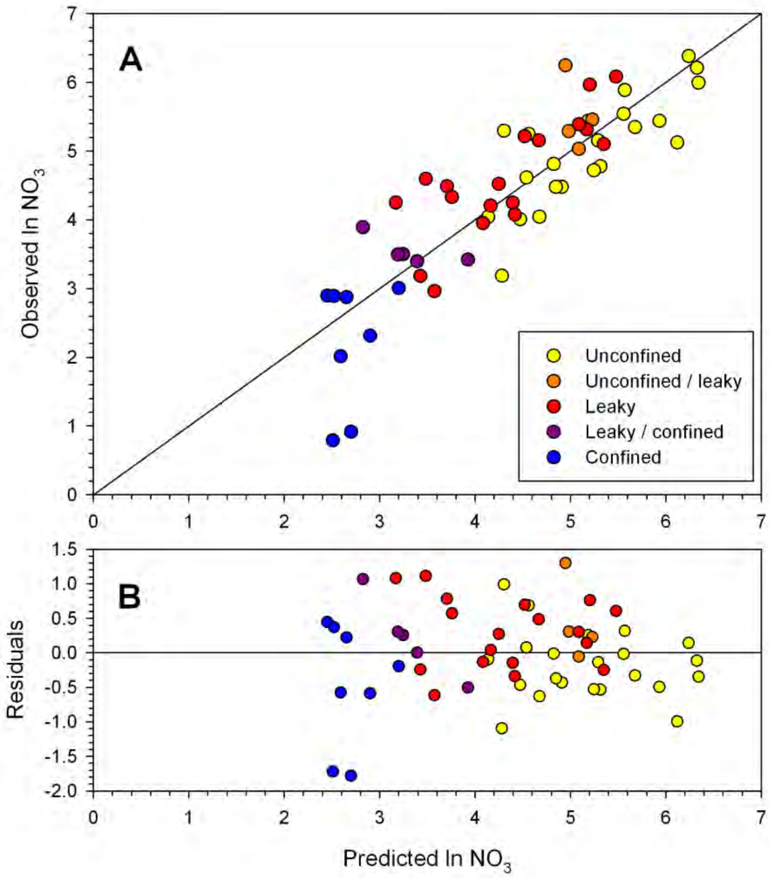


Figure 4.5 *– Relation between observed and predicted log (ln) nitrate concentration (A) with an R^2=0.75, and between residuals and predicted log nitrate concentration (B) for calibration wells.*

4.4.4 – Validation of the model

The MLR model was validated with an independent data set comprising 25 wells sampled in 2005 and 2008 (Menció et al, 2011b) and they were representative of all aquifer types. Nitrate content in those wells ranged from 2 to 180 mg/L. Predicted values for nitrate concentration were calculated for these wells using model parameters in Table 4.2. The observed versus predicted values have an R^2 of 0.53 and a very low p-value of 0.00003, indicating that the model fit is acceptable (Figure 4.6). The fit line is very similar to the 1:1 line. The lower degree of correlation compared to the calibration data set (R^2= 0.75) is related to the limited distribution of the wells, and in the case of confined aquifers, to the uncertainties on the local deep geological setting in the wells' nearby areas and the well-casing characteristics that may facilitate mixing of water from distinct layers with different nitrate concentrations.

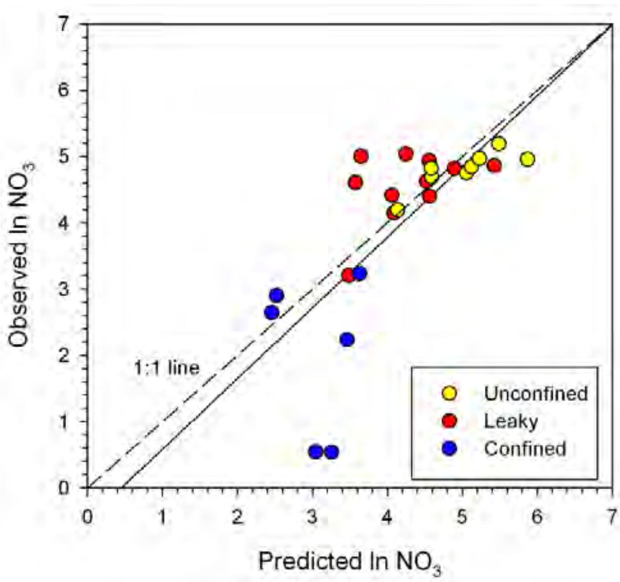


***Figure 4.6** – Relation between observed and predicted log (ln) nitrate concentration with an R^2=0.53 and p-value=0.00003 for validation wells.*

4.4.5 – Vulnerability maps

Nitrate concentration in groundwater was calculated for 10-m grid cells using Eqs. (2) and (3) with the estimated coefficients presented in Table 4.2, resulting in distinct vulnerability maps of the Osona region according to aquifer type (Figure 4.7 for unconfined aquifers, Figure 4.8 for leaky aquifers, and Figure 4.9 for confined aquifers). Coefficients may satisfactorily predict the nitrate content at any location once the calibration procedure has been conducted. Therefore, MLR allows determining the spatial distribution for distinct values of those variables, including the aquifer type expressed as a categorical one. Because this variable was only known at the sampled wells, a vulnerability map for each aquifer type was generated by assigning the appropriate value for this parameter in the regression model. This addressed the different aquifer types found in depth (unconfined, leaky and confined) on a sub-regional scale by enabling model predictions throughout the study area for each aquifer type.

Mapped nitrate concentrations consequently reflect local patterns of nitrogen sources and aquifer susceptibility characteristics. On one hand, vulnerability maps for the unconfined aquifer are fairly intuitive as most of the factors involved in the MLR equation are related to surface processes or characteristics (Figure 4.7). Predicted nitrate concentrations are very high (above 300 mg/L) in the central part of the study region, named Plana de Vic.

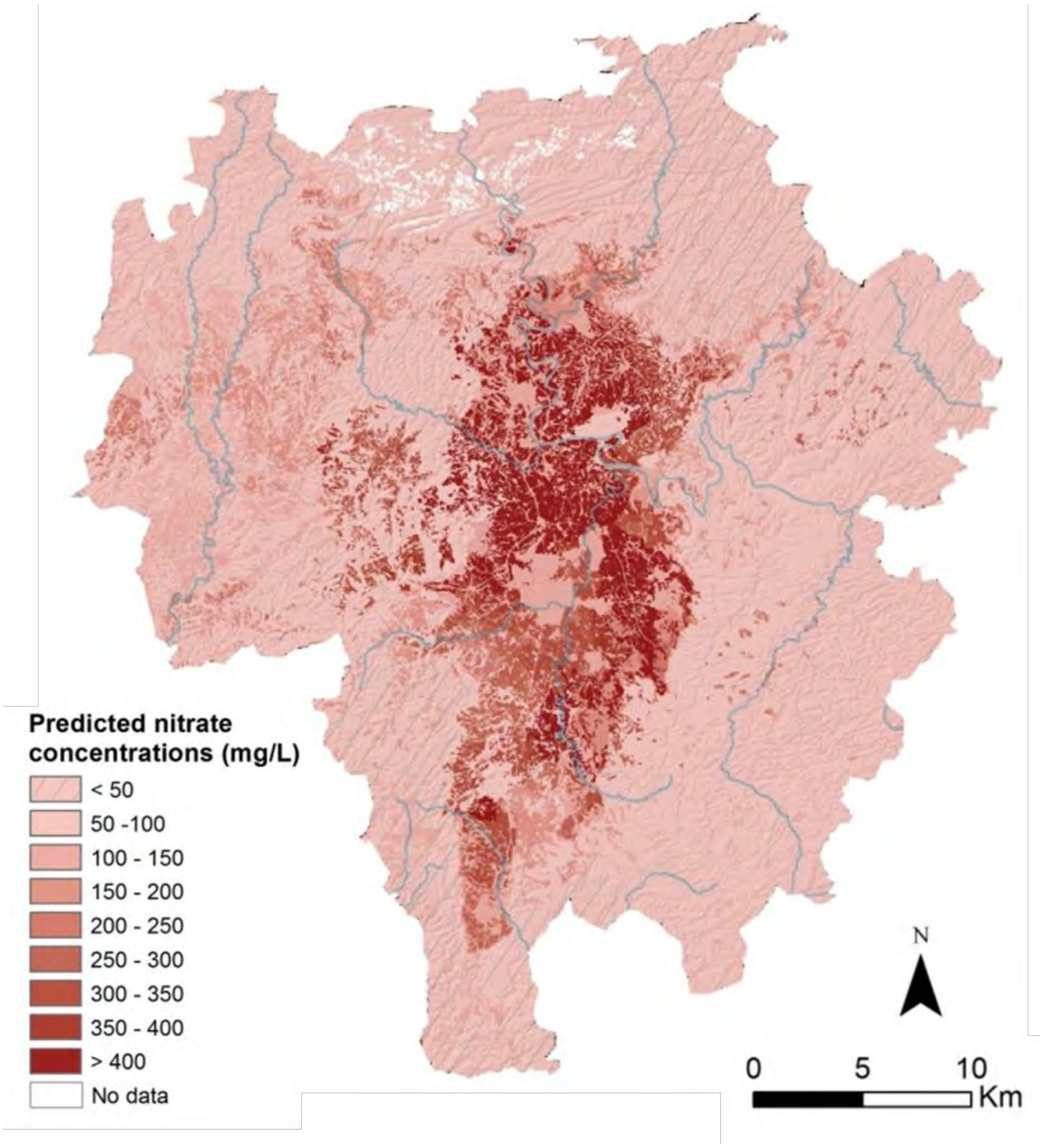


***Figure 4.7 –** Vulnerability map of predicted nitrate concentration for unconfined aquifers in the Osona region. No data refers to missing values of the nitrogen load variable for these areas (see section 4.3.2).*

Alluvial sediments, as the main surface formation, allow the development of deep productive soils suitable for agricultural practices. Moreover, most of the farms are also located in this area and consequently, big amounts of nitrogen manure are produced nearby and used to fertilize these crops. Predicted low nitrate concentrations (below 50 mg/L) dominate in the surrounding areas which are mostly forested, or where denitrification occurs. Notice that the vulnerability map for the unconfined aquifer mimics the nitrogen load and the Haplic Calcisol spatial distributions. However, irrigated areas along the Ter River define a corridor of low predicted nitrate content, as for instance, nearby the municipality of Manlleu, displaying the influence of surface water diverted from the river to the crops.

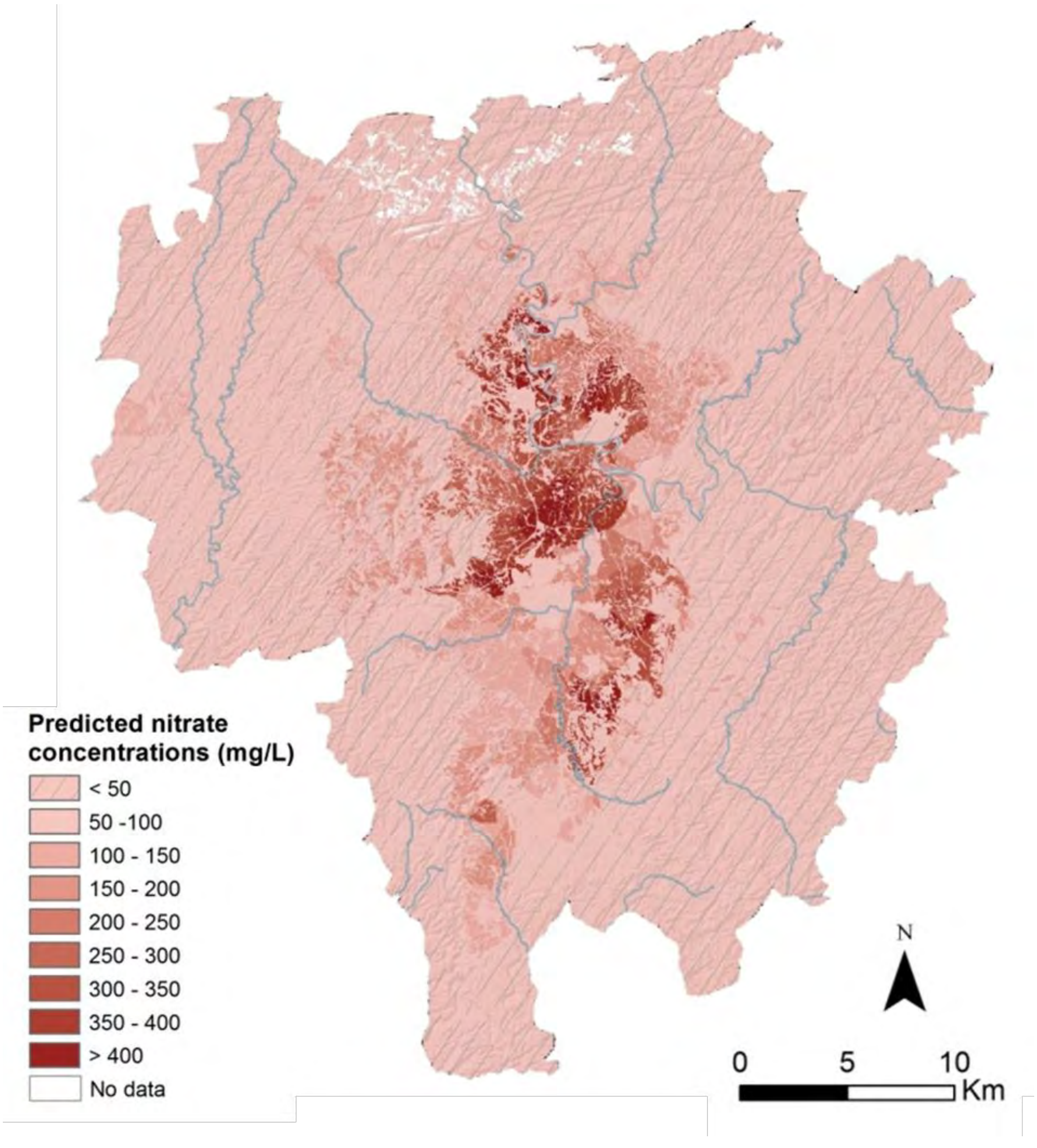


***Figure 4.8** – Vulnerability map of predicted nitrate concentration for leaky aquifers in the Osona region. No data refers to missing values of the nitrogen load variable for these areas (see section 4.3.2).*

On the other hand, each of the five variables selected for the MLR model can be assumed to hold for the entire aquifer column. Such a projection in depth that allows estimating the vulnerability of the underlying aquifer formations, whether leaky or confined, must be conceptually discussed before addressing the outputs of the model. Although it may look like a paradox, wells attributed to confined aquifers have some nitrate content (with a mean concentration of 12.0±2.6 mg NO3/L, notably smaller than that of the wells in leaky, 138.2±27.6 mg NO3/L, and unconfined aquifers, 196.7±31.6 mg NO3/L) due to the incomplete isolation of these layers from the uppermost geological units where manure is applied as fertilizer.

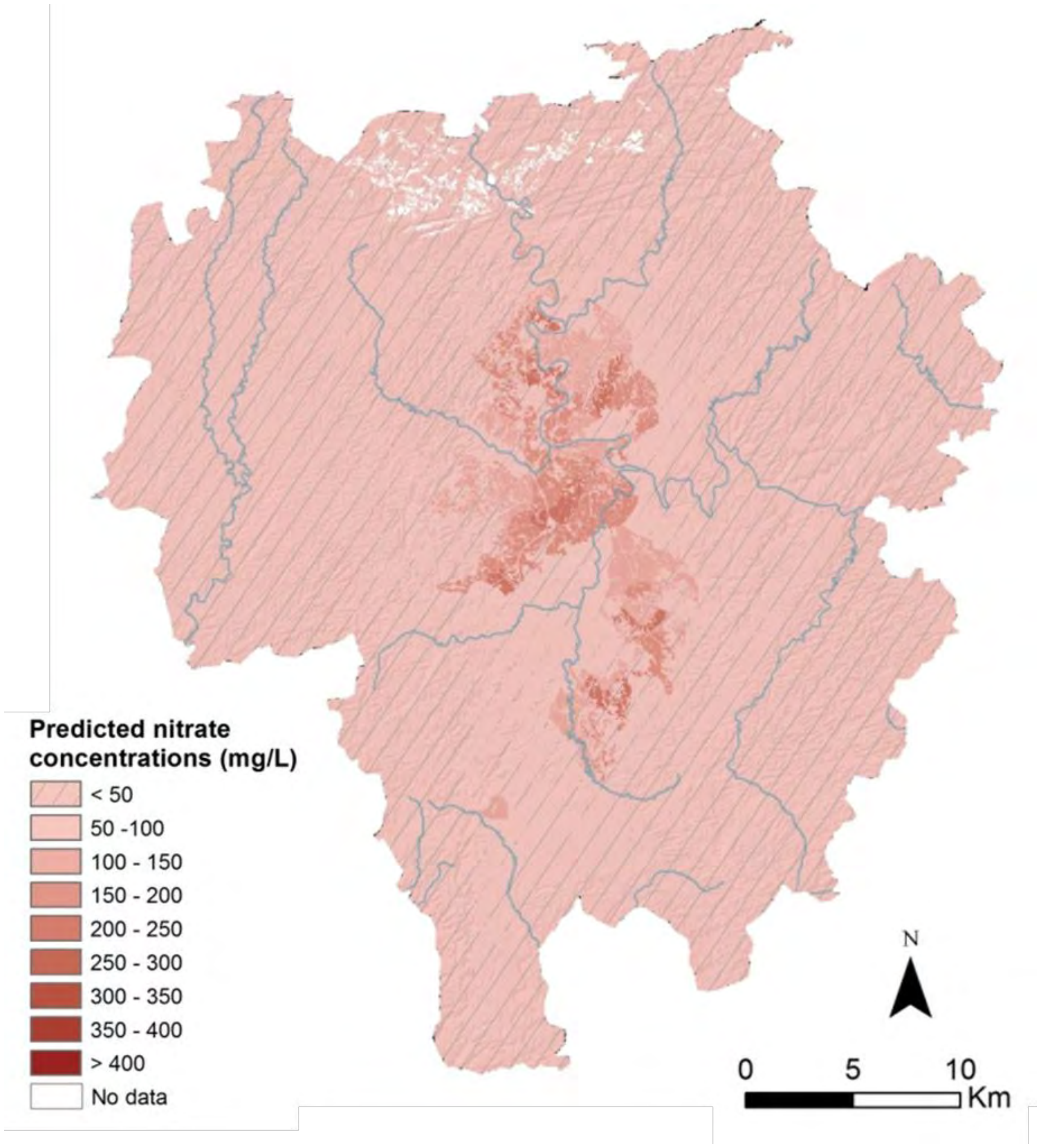


__Figure 4.9 –__ Vulnerability map of predicted nitrate concentration for confined aquifers in the Osona region. No data refers to missing values of the nitrogen load variable for these areas (see section 4.3.2).

Pumping influences on the flow field that develop downward fluxes, and defects on borehole construction inherent to drilling and well-casing, contribute to the occurrence of nitrate in the water samples of wells located in confined aquifers (Menció et al., 2011b). Potential nitrate infiltration in the recharge areas of the confined layers is a less probable explanation, since they lay in distant forested areas with no agricultural activity. Moreover, transit time is expected to be larger than groundwater ages obtained by tritium data, supporting the hypothesis of vertical downward nitrate-rich fluxes as the source of pollutant in the deep confined layers. In this sense, surface processes and geological properties considered in the MLR model will properly determine nitrate concentration in each geological setting.

The vulnerability map for the leaky aquifers mainly reflect the influence on depth of surface soil characteristics and the spatial distribution of nitrogen inputs (Figure 4.8). According to the MLR model, it is assumed that a leaky aquifer exists over all the area at a given depth, which is geologically consistent given the multilayered nature of the hydrogeological system. Furthermore, it has been proved that the fractured marl layers let downward fluxes occur that transport nitrate to the leaky aquifers, as evidenced by the observed mean nitrate concentration in those wells located in leaky aquifers (138.2±27.6 mg NO_3/L). These results are consistent with the high nitrate concentrations (approximately 200 mg/L) predicted in some areas of Plana de Vic, where agricultural and livestock activities are remarkably intensive.

Focusing on the prediction map for confined aquifers (Figure 4.9), nitrate concentrations are lower than the drinking threshold in most of the study area. Although all the wells in confined aquifers used in model calibration were located in the Lluçanès area (western part of the study area), relatively high nitrate concentrations around 100 mg/L are still predicted in the central part of the region, pointing out unsuitable areas for groundwater exploitation. In this sense, this vulnerability map represents the expected nitrate content in depth with the shielding effect of the overlying geological formations. The limited distribution of wells in the confined aquifers and that the MLR is mainly based on surface properties may be the reason because the model is weaker with depth. Therefore, predicted nitrate concentrations for confined aquifers should be carefully evaluated on the light of the geological characteristics of the point of interest.

Working on the vulnerability maps, approximately 90% and 75% of the area for confined and leaky aquifers, respectively, show estimated nitrate contents below 50 mg/L (Figure 4.10). Even though nitrate concentrations for unconfined aquifers cover a wider range, about 70% of the area has predicted concentrations between 50 to 150 mg/L. Nitrate content in agricultural areas are relatively high for unconfined and leaky aquifers. For instance, up to 25% of the area for unconfined aquifers has nitrate concentrations higher than 250 mg/L. These figures point out that most of the Osona region is highly vulnerable to nitrate pollution, especially in agricultural land.

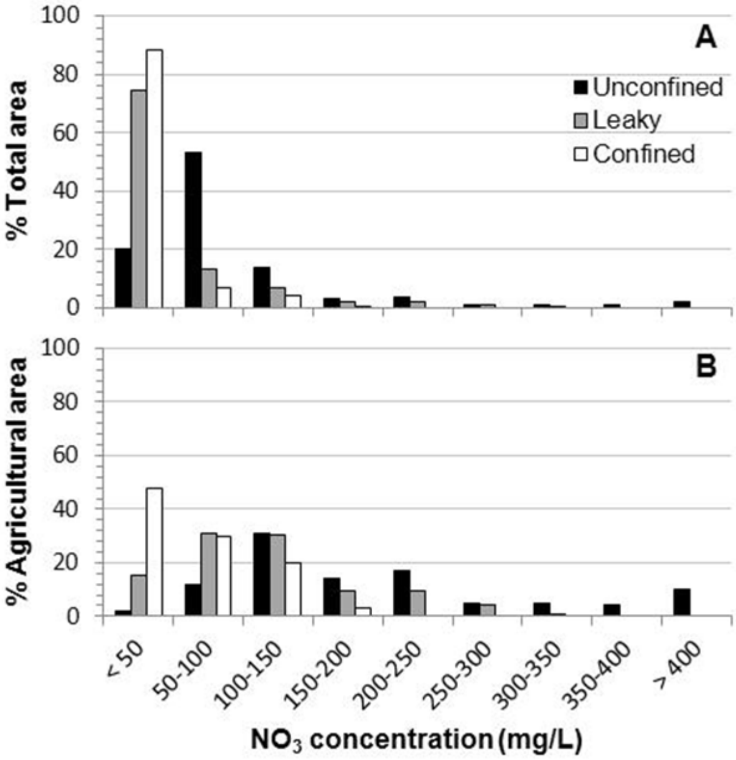


Figure 4.10 *– Percent of surface area of the whole study area, and that of the agricultural land only, for each range of nitrate concentration and aquifer type.*

4.5 – CONCLUSIONS

The multiple linear regression (MLR) model presents predicted nitrate concentration in groundwater given nitrogen inputs and aquifer susceptibility characteristics. The model explains 75% of the variation of nitrate in groundwater in the Osona region (NE Spain). Among many potential explanatory variables to be included in the model, MLR was used to identify those that significantly influence nitrate occurrence. The selected variables were: 1) net nitrogen input as manure, 2) aquifer type, 3) percent well-drained, deep soils, 4) percent irrigated crops, and 5) an indicator of the presence of denitrification processes, which together represent the input of nitrogen, transport of nitrate to aquifers and attenuation processes of nitrate in groundwater. All p-values indicate that the five variables are significant at the 0.10 level. Slope coefficients indicate that nitrate concentration in groundwater are higher with increasing net nitrogen loading, where the wells are located in unconfined aquifers, and with the increasing percent of well-drained deep soils, and lower where stream water is used to irrigate crops and denitrification processes occur.

The model features three innovations: net nitrogen input was determined throughout the region using a simple mass balance approach and a newly available GIS tool (NACT tool); the model addresses the occurrence of distinct aquifer types in depth (unconfined, leaky and confined); and detailed aquifer chemistry at well locations was incorporated into the spatial model by reducing data to composite variables for subsequent interpolation by kriging.

Regarding vulnerability maps, the MLR model predicts high nitrate concentrations (above 300 mg/L) for the unconfined aquifers in the central part of the study area, where most of the agricultural and livestock activity is found and, therefore, large amounts of fertilizer are applied. Low nitrate concentrations (below 50 mg/L) are expected in the surrounding areas with forested land use and in those areas where denitrification processes have been identified, as well as in deep aquifers, especially in the confined ones. Nonetheless, some high nitrate concentrations around 200 mg/L are predicted for leaky aquifers in the central part of the region and in some areas, concentrations about 100 mg/L also for confined aquifers. This may be related to the infiltration of nitrate polluted groundwater from upper unconfined aquifers to the lower layers, induced by excessive pumping and deficiencies in well casing.

Considering the aquifer type as an exploratory variable allows drawing vulnerability maps for the unconfined, leaky and confined aquifers. In this case, the model implicitly recognizes than nitrate occurrence in depth is related to fertilization practices on the surface and to the buffering effect of aquitards on the leaky aquifer recharge. Therefore, these maps provide a valid estimate that allows water managers prioritize areas for groundwater monitoring and exploitation.

Finally, further development of the model may be used to evaluate the effect on groundwater pollution of alternative agricultural management practices. Because it predicts nitrate concentrations, the model could be also used for exposure estimate in epidemiological studies on the effect of polluted groundwater on human health.

CHAPTER 5

General discussion

Nitrate pollution in groundwater is a major concern in the Osona region. Nitrate contents above 50 mg/L are commonly found, reaching up 450 mg/L in some of the sampled wells and springs. In most of the studies conducted to describe the occurrence of nitrate in groundwater use water samples from wells. In the effort to characterize nitrate dynamics, this dissertation explores the suitability of spring water as a potential indicator of shallow groundwater systems quality. For this reason, several springs in the study area were geologically characterized, and their hydrologic and hydrochemical responses to rainfall and land use were investigated, in order to understand nitrate recharge processes to aquifers. However, one cannot overlook water wells, since they are an important source for drinking water supply, as well as for other uses. In particular, springs are useful tools to investigate nitrate inputs to the system, and wells to delineate vulnerability maps based on the actual nitrate concentration that finally reach water users.

There are advantages and disadvantages of sampling water from springs and wells. On one hand, springs are usually representative of subsurface flows in their nearby recharge areas. On the other hand, wells are indicative of a larger portion of the aquifer including shallow and/or deep groundwater flows. Wells, however, are inherent of each sampled point and their water characteristics depend on well-construction and casing. In the Osona region, wells are typically constructed of multiple casing strings or are simply open boreholes. Consequently, water samples represent a mixing of waters from the different aquifers layers where the well is drilled. Moreover, wells are influenced by withdrawals rates which modify water flow; whereas, in general, springs are only affected by natural variations. Therefore, the study of nitrate occurrence in groundwater requires considering the complexity of the geological system, together with different scales of groundwater flow paths; that is, subsurface flows to springs and larger deeper flows to wells in unconfined, leaky and confined aquifers. Consequently, nitrate pollution in groundwater is herein addressed by monitoring springs and wells, and by a join evaluation of the results of both datasets.

Many factors affect the migration of nitrate in groundwater, comprising the intensity and distribution of fertilizer and manure use, land management practices and other anthropogenic activities; as well as natural factors, such as soil and aquifer characteristics, hydrology, and the chemical properties of the nutrients compounds themselves. Therefore, the study of the occurrence and transport of nitrate in groundwater requires acknowledgment of complex relationships among those different variables. To fulfill this goal, field data are used to build up conceptual models for spring and aquifer processes; and statistical and regression analyses are used to identify the key factors that significantly influence nitrate concentration in groundwater and, finally, to assess groundwater vulnerability to nitrate pollution in the Osona region.

Statistical methods range from simple descriptive statistics of hydrochemical data and physical-chemical parameters to more complex regression analyses that include the effects of several predictor variables. In this work, ANOVA and logistic regression analyses are performed to identify the relevance of land use and geological setting in nitrate pollution in springs (Chapter 2). Exploratory data analysis is also conducted to describe patterns in springs and to investigate the relations between discharge, EC and nitrate content from a hydrologic perspective. Furthermore, a geostatistical analysis of discharge and nitrate time-series using variograms permitted to identify different temporal trends and to describe how temporal continuity changes as a function of time lags (Chapter 3). The relationship between nitrate concentration in groundwater and several explanatory variables is investigated using a multiple linear regression model that will allow creating vulnerability maps (Chapter 4). Geographical Information Systems (GIS) are used for mapping nitrate concentrations and different variables in the Osona region, as well as for evaluating groundwater vulnerability parameters using specific GIS tools.

Focusing on the data, nitrate concentration in natural springs in the Osona region has been recorded twice a year since 2004 by the local authorities (Consell Comarcal d'Osona). In the first study of this PhD dissertation (Chapter 2), 131 out of 400 springs were selected from a large database, based on their geological setting representativeness, sampling frequency and nitrate concentration range. This historical record of nitrate data in springs provides a general overview of the nitrate problem in groundwater, and it also describes spring water pollution depending on geological setting and land use in the recharge area. Springs were hydrogeologically classified to investigate which geological features might control nitrate occurrence and transport (Figure 2.2). Despite the lack of more accurate methods, approximate recharge areas of each spring were drawn according to its geological context and adjacent topography.

Some of the factors that are believed to most influence nitrate pollution in groundwater are land uses and geology. ANOVA and logistic regression analysis point out that nitrate concentration is more dependent on land use than on the geological setting of springs (Figures 2.3-2.5). Results report that land use, especially agricultural land, plays an important role in determining the magnitude of nitrate pollution in groundwater. Springs located in agricultural areas with intensive fertilization (mainly in Plana de Vic) have higher nitrate concentration than those situated in areas with fewer crops and forests (Lluçanès area, and the surroundings of la Plana). It seems evident that land uses affect groundwater quality, but this statistical analysis concludes that geology is not a factor that significantly controls nitrate concentration in springs. Consequently, it is not possible to define which geological characteristics influence nitrate inputs to soil water and by extension to aquifers, using this dataset and these statistical methods.

Nevertheless, this database on nitrate data from springs was used to depict its background concentration. Background levels represent the amount of naturally occurring chemical substances derived from natural processes in the environment. Nitrate background concentrations in the Osona region show a threshold value of 7-8 NO_3^- mg/L, meaning that nitrate concentrations above 8 mg/L indicate anthropogenic influence on groundwater quality. The identification of this background level was focused only on those springs located in sedimentary materials, following the methodological requirement to ensure a relative homogeneity of the data. Therefore, background levels are only an indicative measure of the initial nitrate content in pristine areas, and should not be considered as a goal for aquifer remediation actions. Nowadays, it seems unrealistic to reach back these initial values because of the complexity of the hydrogeological system and the high nitrate concentrations found in groundwater in the study area, after decades of fertilization.

In this initial analysis of spring data, factors that govern nitrate occurrence and evolution in groundwater could not be precisely depicted because of the long time between each sampling campaign in this dataset. For this reason, 13 springs were selected for a periodic survey over one year (January 2010 – February 2011; Chapter 3). Discharge, electrical conductivity (EC), nitrate concentration, pH value and water temperature were monitored every two weeks. Moreover, two extensive hydrochemical analyses were conducted at the beginning and at the end of the survey. Even though most of the selected springs are located in the central part of Osona, where nitrate concentrations in groundwater are higher, these sampled springs are representative of all existing geological settings, land uses and nitrate content ranges in the area. Therefore, temporal trends observed in those springs are illustrative of different hydrological behaviors, and they can be extrapolated to other springs with similar features. At the end, four distinct hydrologic response types (HRT) based on discharge, EC and nitrate data summarize the hydrological behavior of springs (Table 3.3).

This more detailed dataset suggests that geological setting has little effect on nitrate infiltration to groundwater. Nitrate-rich recharge equally affects both surface hydrogeological layers, concentrated in quaternary sedimentary formations, and deeper aquifers, constituted by fractured marls and sandstone formations, which form the basement of the quaternary deposits. According to the time-plots (Figures 3.4-3.7), discharge and EC show a consistent behavior determined by the distinctive hydrogeological dynamics of each HRT. In contrast, nitrate concentration generally appeared uniform over time with only minor influences from external factors, such as major rainfall events. Geostatistical analyses (variograms) also support this finding. In particular, EC changes in spring water over time indicate water-rock interaction and dilution processes along the pathway from the recharge area to its output in the spring. These changes also depend on whether spring discharge is only determined by the draining of surface deposits (shallow flow lines) or by flow paths from the underlying formations as well (deep flow lines). Springs located in pre-quaternary and quaternary sediments (mainly alluvial) presented a more variable discharge and EC throughout time, which indicates their sensitivity to the rainfall regime. Oppositely, nitrate appears to be buffered by hydrogeological and hydrogeochemical processes, as well as by decades of intensive inputs to the subsurface, showing a lack of correlation with seasonal events, as meteorological or fertilization periods.

These results indicate that land uses and agricultural practices, especially the amount of applied organic fertilizer, determines the magnitude of nitrate content in springs in Osona. The uniform nitrate concentration over time observed in most of the monitored springs suggests a homogenization of the subsurface processes that finally govern nitrate infiltration to groundwater. Assuming that spring data are hence representative of nitrate leaching towards the underlying aquifer, nitrate content of infiltrating recharge to shallow aquifers should thus present a steady value over time with only small fluctuations due to natural processes, as heavy rainfall events.

Indeed, the influence of rainfall to spring hydrochemistry was also observed when comparing nitrate concentration in different seasons (spring and fall) and years, using the first dataset that covers from 2004 to 2009 (Figure 2.3). In general, an increase in nitrate content was mainly associated to heavy rainfall periods, while it tended to decrease during long dry periods. However, logistic regression analysis showed that sampling campaign (that is, seasonality) did not have a significant influence on nitrate pollution. This statistical finding is in agreement with the steady nitrate values observed during the more detailed survey conducted in 2010-2011.

Another variable that could influence nitrate content in springs is the fertilization regime. Manure and slurry are usually spread on the crops as organic fertilizer during specific periods of the year depending on crop type. Nevertheless, it also depends on the convenience of the farmer and the amount of fertilizer stored in the farm ponds. Temporal variations of nitrate as concentration peaks associated with fertilization episodes are not clearly observed. As mentioned, the homogenization effect of hydrogeological and geochemical processes in the soil and in the aquifer prevents fertilization from a sudden increase in nitrate content in recharge flows. This is also attributed to the amount of nitrate stored in the soil and in the aquifers after decades of fertilization. Consequently, a potential cease of fertilization, however unimaginable, would not immediately reduce nitrate infiltration to groundwater. A noticeable response of decreasing nitrate concentrations in springs would only be expected after several years, and even in a longer time span (decades) in wells.

Hydrologic and hydrochemical responses of springs provide evidence about nitrate recharge to aquifers. Additionally, groundwater management in polluted areas must pay attention to the actual nitrate levels in depth (that is, those from well water samples) as they constitute the water supply for human consumption. Therefore, a link between nitrate concentration and those factors that control its magnitude must be sought to understand the extent of the pressures upon groundwater quality and how the hydrogeological systems respond to them. Regression models constitute an appropriate approach to deal with this issue. Once the relationships have been established, nitrate concentration can be simulated for distinct scenarios and mapped to draw vulnerability maps necessaries to manage local water resources.

A total of 63 wells in the Osona region were also sampled for hydrochemical analyses in May 2010. The selection of wells was done based on information from existing databases and it was aimed to include wells with different depths, land uses in their capture areas, and several nitrate content ranges. In order to assess groundwater vulnerability, nitrate data from wells was integrated into a multiple linear regression (MLR) model together with several explanatory variables to investigate which of them, whether anthropogenic or natural, determine nitrate concentration and their relevance. This set of variables included some of the parameters already used in the previous logistic regression analysis, such as land use, geology and hydrochemical data. Additionally, other information representing the input of nitrogen (e.g.: manure applied and crop nitrogen uptake), transport (e.g.: soil properties and climate data) and attenuation (e.g.: denitrification processes) were incorporated into the model (Table 4.1). A principal components analysis (PCA) of groundwater chemistry, isotope data (from references), and physical-chemical parameters was performed to identify hydrological processes and, more importantly, to create a composite variable that represented all chemical parameters for inclusion into the regression model. Moreover, it was sought that all these explanatory variables could be mapped to create vulnerability maps. In order to accommodate the complexity of the hydrogeological system, the aquifer vertical layering was considered in the model by adding a variable that distinguished the aquifer type where the well was located (namely, unconfined, leaky or confined aquifer types).

According to the MLR model, the variables that most influence nitrate pollution are nitrogen loading as manure, aquifer type, presence of well-drained and deep soils, existence of irrigation and occurrence of denitrification processes (Table 4.2). These variables are interrelated and explain the amount of nitrate to groundwater at satisfactory p-value levels (<0.10). As already observed in the logistic regression analysis, agricultural land use (expressed in the MLR as nitrogen load) is one of the most important factors that control the amount of nitrate concentration in groundwater. Most of the agriculture is developed on well-drained and deep soils, related to the occurrence of alluvial sediments. The use of low-nitrate surface water to irrigate some of these crops generates a dilution effect within the aquifer and, therefore, a decrease in its nitrate content. Aquifer type and natural attenuation were also represented in the model. All these variables allow estimating nitrate distribution in the distinct aquifer types. Nitrate concentration can thus be predicted in areas where there are no monitoring wells, by applying the regression equation with the estimated coefficients for the selected variables.

Mapped nitrate concentrations reflect local patterns of nitrogen sources and aquifer susceptibility characteristics. Nitrate is present in all aquifer types (Figure 4.7). In the unconfined ones is a result of direct infiltration; in the confined aquifers is because of their incomplete isolation from the uppermost geological formations, where manure is applied, due to defects on borehole construction. In this sense, the vulnerability map for the unconfined aquifer is fairly intuitive, as most of the factors involved in the MLR are related to surface processes. Nevertheless, the regression model is valid for leaky and confined aquifers as well. However, special attention should be put on the interpretation of vulnerability maps in deep layers. In this sense, it must be recalled that each variable in the regression model is assumed to hold for the entire aquifer and such a projection in depth permits estimating the vulnerability of the underlying aquifer formations, whether leaky or confined. The categorical value given to each well, according to its aquifer type, corrects the estimation of the coefficient for the depth factor. This coefficient is thus valid for any aquifer type as it has been optimized in consonance with the actual nitrate concentration together with the other variables included in the MLR. This variable stands as the most significant variable as it has the lowest p-value. Then, vulnerability maps for leaky and confined aquifers represent the expected nitrate content in depth, resulting from surface nitrogen inputs and the buffering effect of the upper geological formations due to, 1) the low vertical hydraulic conductivity, that governs downward fluxes from the surface, and 2) geochemical processes as denitrification.

Therefore, the MLR model can be reasonably used as a predictor for nitrate concentration in groundwater for any aquifer type. Vulnerability maps are indicative of the quality of groundwater subjected to current pressures on the environment and water resources. It should be kept in mind that this is a steady-state model because data from groundwater extraction regimes were not available and could not be integrated in the model.

From here on, new scenarios can be drawn to predict potential concentrations of nitrate in the Osona region. For instance, simulating how groundwater quality would be affected by incorporating new alternative management practices. Vulnerability maps can help managers on deciding the best location for drilling a new well; just by looking at those areas that are less sensitive to contamination. However, a local-scale hydrogeological study should be conducted to assess the appropriateness of aquifer exploitation at a given site while preserving the aquifer groundwater quality from nitrate pollution.

CHAPTER 6

General conclusions

The study of springs and wells to characterize nitrate occurrence and the identification of the factors that most influence groundwater vulnerability to nitrate pollution using statistical and regression analysis is summarized in the following conclusions:

- Springs are valuable indicators of shallow groundwater systems quality, and together with well data, allow characterizing nitrate occurrence and the hydrodynamics of the aquifer systems.
- Nitrate background concentrations in Osona presented a threshold value of 7-8 mg/L, meaning that nitrate concentrations above 8 mg/L indicate anthropogenic influence on groundwater quality.
- Logistic regression and ANOVA analyses showed that nitrate pollution in springs is more dependent on land use than the geological setting of springs. Accordingly to this, land use, and particularly fertilization practices, is a major factor that determines groundwater vulnerability to nitrate pollution.
- Four distinct hydrologic response types (HRT) based on discharge, EC and nitrate data summarize the hydrological behavior of springs. Those HRT permit simplifying the diversity of spring hydrogeological settings and, therefore, a more comprehensive interpretation of the hydrological processes is reflected by natural springs.
- Nitrate concentration in springs is fairly constant over time and its magnitude is determined by the land use. The uniform nitrate concentration over time observed in most of the monitored springs suggests a homogenization of the subsurface processes that determine nitrate infiltration after decades of intensive fertilization using pig manure and slurry. Moreover, temporal variations on nitrate concentrations due to fertilization regimes were not clearly observed.
- Electrical conductivity and discharge are related to specific hydrogeological behaviors and their variations over time are controlled by the geological setting, as well as by major rainfall events.
- Assuming that spring data are representative of nitrate leaching towards the underlying aquifer, nitrate content of infiltrating recharge in the Osona aquifers should therefore show a steady value over time with only small fluctuations due to natural processes.
- A multiple linear regression (MLR) model integrating nitrate data from wells together with several explanatory variables, representing nitrogen sources, transport and attenuation, permitted assessing nitrate groundwater vulnerability. The MLR model determined the factors that significantly influence nitrate pollution, which are: nitrogen load as manure,

aquifer type, presence of well-drained and deep soils, irrigation and occurrence of denitrification processes.

- The MLR model featured three methodological innovations: net nitrogen input was determined throughout the region using a mass balance approach and a newly available GIS tool; the model addressed vertical aquifer layering; and detailed aquifer chemistry at well locations was incorporated into the model by a principal component analysis (PCA), in order to obtain a composite variable for subsequent interpolation by kriging.
- Vulnerability maps for unconfined, leaky and confined aquifers were developed according to the calibrated regression model and reflect local patterns of nitrogen sources and aquifer susceptibility characteristics. These maps allow identifying areas susceptible to nitrate contamination.

Finally, the findings of this dissertation complement previous studies and allow drawing a hydrogeological conceptual model that describes nitrate pollution in groundwater in the Osona region. This model, together with other tools as the vulnerability maps presented in this doctoral thesis, become useful for groundwater protection planning, management and decision making. The main features of this hydrogeological conceptual model are as follows:

1) Groundwater nitrate pollution is a common concern in most parts of the Osona region, especially in the central part of Plana de Vic, because of its high levels and widespread distribution. It is proved that the main source of nitrate is pig manure (Vitòria, 2004; Otero et al., 2009; Menció et al, 2011b).
2) Nitrate background concentrations in Osona show a threshold value of 7-8 mg NO_3^-/L, meaning that nitrate concentration above 8 mg/L indicates anthropogenic influence on groundwater quality (Menció et al., 2011a, in Chapter 2 of this doctoral thesis).
3) Nitrate concentration in wells depends on the exploited aquifer layer. Nitrate content in those wells located in shallow unconfined aquifers depends directly on the amount of fertilizer applied on the crops. However, nitrate in deep wells is due to a mixing between flows from different layers as most of the boreholes are uncased and are connected to distinct aquifers. Downward fluxes created by pumping wells are responsible for the nitrate content in deep aquifer layers, whether leaky or confined, which are incompletely isolated due to the fractured nature of the confining layers and the inappropriate well construction (Menció et al., 2011b).
4) A detailed characterization of springs identifies a continuous and uniform nitrate input to groundwater, with only a minor influence from natural external factors such as heavy rainfall events. The evenness of this infiltrating mass is attributed to a homogenization of

the subsurface processes that determines nitrate infiltration after decades of intensive fertilization (Boy-Roura et al., 2013, in Chapter 3 of this doctoral thesis).

5) Statistical and regression analyses have identified the variables that determine the occurrence of nitrate pollution in groundwater. Results point out that nitrate concentration is more dependent on land use than on the geological setting of springs. Geology is not a factor that significantly controls nitrate concentration in springs (Menció et al., 2011a; Chapter 2 of this dissertation). In particular, impacts on groundwater quality are mainly related to intensive agricultural and livestock activities, which generate large amounts of organic fertilizer that are later on applied to the crops. Contrarily, irrigation with surface water dilutes nitrate content (Boy-Roura et al., submitted, in Chapter 4 of this doctoral thesis).
6) Nitrate isotopic data suggests that denitrification processes are taking place, mainly due to pyrite oxidation (Vitòria, 2004) and by organic matter oxidation (Otero et al., 2009; Torrentó, 2010). An approximation of the degree of natural attenuation has been performed in those samples presenting clear denitrification, and a median value of 30% of contaminant diminution was obtained. However, due to the high nitrate concentrations in groundwater, denitrification processes are not sufficient to intensely reduce nitrate concentration to very low concentrations. Laboratory and field-scale experiments suggest that induced biodenitrification could be applied to some extent as a remedial alternative to enhance natural attenuation in this area (Torrentó et al., 2011; Vidal-Gavilan et al., 2013).

In synthesis, groundwater nitrate pollution in groundwater in the Osona region is a persistent and widespread problem, as observed in the field and as reflected by the vulnerability maps. In order to prevent a further deterioration of water resources, groundwater with current good quality (especially deep aquifers) should be protected from human pressures, such as fertilizer application or excessive groundwater withdrawal. An improvement of groundwater quality is not expected, unless future pressures on the environment and water resources (especially agricultural and livestock activities) reduce their extension and intensity (e.g.: amount of nitrogen fertilizer applied on crops). However, because of the long residence times of groundwater in aquifers and the current high nitrate concentrations, a decrease in nitrate content in groundwater is not foreseen until many years (decades) from now.

References

Abad, A., 2001. Paleotaxodonta y pteriomorphia del eoceno del margen sur de la depresión central catalana. PhD dissertation. Universitat Autònoma de Barcelona.

ACA (Agència Catalana de l'Aigua), 2005. Caracterització de masses d'aigua i anàlisi del risc d'incompliment dels objectius de la Directiva Marc de l'Aigua (2000/60/CE) a Catalunya (conques intra i intercomunitàries) - Document IMPRESS. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona.

ACA (Agència Catalana de l'Aigua), 2007. Evolució i estat de les aigües subterrànies de Catalunya a conseqüència de la contaminació per nitrats. Autors: Niñerola, J.M., Iglesias, M., Fraile, J., Floría, E., Garrido T. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona.

ACA (Agència Catalana de l'Aigua), 2010a. Estimació i prognosi de la demanda d'aigua a Catalunya. Bases tècniques. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona.

ACA (Agència Catalana de l'Aigua), 2010b. Pla de gestió del districte de conca fluvial de Catalunya. Generalitat de Catalunya, Departament de Medi Ambient i Habitatge. Barcelona.

ACA (Agència Catalana de l'Aigua), 2012. Xarxes de control del medi. http://aca-web.gencat.cat/sdim/visor.do [last accessed 08/10/2012].

Addiscott, T.M., Whitmore, A.P., Powlson, D.S., 1991. Farming, fertilizers and the nitrate problem. CAB International. Wallingford, UK. 176 p.

Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., 1985. DRASTIC- A standardized system for evaluating ground water pollution potential using hydrogeologic settings. U.S. Environmental Protection Agency report EPA/600/2-85/018, pp. 163.

Amiel, R.B., Grodek, T., Frumkin, A., 2010. Characterization of the hydrogeology of the sacred Gihon Spring, Jerusalem: a deteriorating urban karst spring. Hydrogeol J 18: 1465-1479.

Antonakos, A.K., Lambrakis, N.J., 2007. Development and testing of three hybrid methods for the assessment of aquifer vulnerability to nitrates, based on the drastic model, an example from NE Korinthia, Greece. J. of Hydrology 333: 288-304.

Barnes, R., 2003. Variogram Tutorial. Golden CO Golden Software.

Bauer, I., Bor, J., 1995. Lithogene, geogene und anthropogene Schwermetallgehalte von Lößböden an den Beispielen von Cu, Zn, Ni, Pb, Hg und Cd. Mainzer Geowiss Mitt 24 :47–70

Bauer, I., Bor J., 1993. Vertikale Bilanzierung von Schwermetallen in Böden – Kennzeichnung der Empfindlichkeit der Böden gegenüber Schwermetallen unter Berücksichtigung von lithogenem Grundgehalt, pedogener An- und Abreicherung sowie anthropogener Zusatzbelastung, Teil 2. Texte 56 Umweltbundesamt, Berlin.

Bauer, I., Sprenger, M., Bor, J., 1992. Die Berechnung lithogener und geogener Schwermetallgehalte von Lößböden am Beispiel von Cu, Zn und Pb. Mainzer Geowiss Mitt 21: 7–34.

Böhlke, J.K., 2002. Groundwater recharge aquifer contamination. Hydrogeol J 10:153–179.

Boy-Roura, M., Menció, A., Mas-Pla, J., 2013. Temporal analysis of spring water data to assess nitrate inputs to groundwater in an agricultural area (Osona, NE Spain). Science of the Total Environment 452-453, 433-445.

Burg, A., Heaton, T.H.E., 1998. The relationship between the nitrate concentration and hydrology of a small chalk spring, Israel. J. of Hydrology 204, 68-82.

Busquets, P., Domínguez, A., Vilaplana, M., 1979. *Geologia d'Osona*. EUMO Pub, Vic, Barcelona.

Buzek, F., Kadlecova, R., Zak, K., 1998. Nitrate pollution of a karstic groundwater system. Isotope Techniques in the Study of Environmental Change, International Atomic Energy Agency Report 1024, Vienna, Austria, pp. 453–464.

CADS (Consell Assessor pel al Desenvolupament Sostenible), 2008. Informe per a la millora de la gestió dels purins porcins a Catalunya. Author: M. Rosa Teira Esmatges; Ed.: Joan-Maria Romaní. Informe del CADS: 5. Generalitat de Catalunya.

Carbó, Ll., Flores, M.C., Herrero, M.A., 2009. Well site conditions associated with nitrate contamination in a multilayer semiconfined aquifer of Buenos Aires, Argentina. Environ Geol 57: 1489-1500.

Catalan Parliament, 2009. Decret 136/2009 d'aprovació del programa d'actuació aplicable a les zones vulnerables en relació amb la contaminació de nitrats que procedeixen de fonts agràries i de gestió de les dejeccions ramaderes. DOGC num. 5457.

Chen, H., Druliner, D., 1988. Agricultural Chemical Contamination of Ground Water in Six Areas of the High Plains Aquifer, Nebraska. National Water Summary 1986—Hydrologic Events and Ground Water 295 Quality. Water-Supply Paper 2325. Reston, Virginia, U.S. Geological Survey.

Clarke, R., Lawrence A., Foster S., 1996. Groundwater: A threatened resource. United Nations Environment Programme, Nairobi, Kenya, UNEP Environment Library No. 15, pp. 15-30.

CREAF, 2011. MCSC (Mapa de Cobertes del Sòl de Catalunya) E: 1:5,000; 3a Edició 2005-2007. Barcelona, Centre de Recerca Ecològica i aplicacions Forestals.

DARP (Departament d'Agricultura, Ramaderia i Pesca), 2000. Manual del codi de bones practiques agràries: nitrogen. Authors: Boixadera, J., Sió, J., Àlamos, M., Torres, E. Barcelona, Generalitat de Catalunya.

DAAM, 2011a. SIR (Sistema d'Informació Ramadera). Barcelona, Departament d'Agricultura, Ramaderia, Pesca, Alimentació i Medi Natural, Generalitat de Catalunya.

DAAM, 2011b. SIGPAC (Sistema d'Informació Geogràfica de Parcel·les Agrícoles). Barcelona, Departament d'Agricultura, Ramaderia, Pesca, Alimentació i Medi Natural. Generalitat de Catalunya.

Danish EPA, 2000. Aquatic Environment 1999. State of the Danish Aquatic Environment. Environmental Investigations No. 3, 2000. 138 p.

Davison, C.C., Vonhof, J.A., 1978. Spatial and temporal hydrochemical variations in a semiconfined buried channel aquifer: Esterhazy, Saskatchewan, Canada. Ground Water 16: 341-351.

De Stefano, L., Llamas, M.R. (Eds.), 2013. Water, agriculture and the environment in Spain: can we square the circle? CRC Press/Balkema, Taylor & Francis Group, London, UK.

Dietrich, P.G., Hebert, D., 1997. Regional discharge of a Triassic artesian karst aquifer: mixing and age of spring waters in the Thuringian basin, Germany, estimated by isotope methods, in: Gunay G, Johnson AI (eds), Karst Waters and Environmental Impacts. A.A. Balkema, Rotterdam, pp. 221–229.

Duan, N., 1983. Smearing estimate: A nonparametric retransformation method. Journal of the American Statistical Association 78, 383, 605-610.

Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton P.A., Hitt, K.J., Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr, N.E., Sprague, L.A., and Wilber, W.G., 2010. The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004: U.S. Geological Survey Circular 1350, 174 p.

EC (European Communities), 1991. Council Directive 91/676/EC concerning the protection of waters against pollution caused by nitrates from agricultural sources (Nitrate Directive). Official Journal of the European Communities, OJ L 375.

EC (European Communities), 2000. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy (Water Framework Directive). Official Journal of the European Communities, OJ L 327.

EC (European Communities), 2006. Directive 2000/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration (Groundwater Directive). Official Journal of the European Communities, OJ L 372.

EEA (European Environment Agency), 1999. Groundwater quality and quantity in Europe. Environmental assessment report No 3. Copenhagen, Denmark.

EEA (European Environment Agency), 2003. Europe's Environment: State of the environment report, 3rd assessment, Environmental Assessment Report No. 10. Copenhagen, Denmark.

EEA (European Environment Agency), 2009. Water resources across Europe – confronting water scarcity and drought. EEA Report, No 2/2009. ISSN: 1725-9177. Copenhagen, Denmark.

EEA (European Environment Agency), 2012. European waters – assessment of status and pressures. EEA Report, No 8/2012. ISSN: 1725-9177. Copenhagen, Denmark.

Elhatip, H., Afsin, M., Kusçu, I., Dirik, K., Kurmaç, Y., Kavurmaci, M., 2003. Influences of human activities and agriculture on groundwater quality of Kayseri-Incesu-Dokuzpinar springs, central Anatolian part of Turkey. Environ Geol 44: 490-494.

EU (European Union), 2010. The EU Nitrates Directive. Fact Sheet. Publications Office. European Comission.

FAO, 2013. AQUASTAT database, Food and Agriculture Organization of the United Nations (FAO). http://www.fao.org/nr/water/aquastat/main/index.stm [last accessed 08/04/2013].

FAOSTAT, 2013. The Statistics Division of the Food and Agriculture Organization of the United Nations (FAO). http://faostat3.fao.org/home/index.html [last accessed 08/04/2013].

Fetter, C.W., 1994. Applied Hydrogeology. Englewood Cliffs, NJ: Prentice-Hall.

Focazio, M.J., Plummer, L.N., Bohlke, J.K., Busenberg, E., Bachman, L.J., Powars, D.S., 1998. Preliminary estimates of residence times and apparent ages of groundwater in the Chesapeake Bay Watershed, and water-quality data from a survey of springs. U.S. Geological Survey Water-Resources Investigations Report, pp. 97 - 4225.

Focazio, M.J., Reilly, T.E., Rupert, M.G., Helsel, D.R., 2002. Assessing ground-water vulnerability to contamination–Providing scientifically defensible information for decision makers: USGS Circular 1224, 33 p.

Freeze, R.A., Cherry, J.A., 1979. Groundwater. Prentice-Hall Inc. Englewood Cliffs, NJ. 604 p.

GDT (Grup de Defensa del Ter), 2005. Les fonts que tenim: Osona i el Lluçanès. Eumo Editorial, Vic, Spain.

Gich M., 1972. Estudio geológico del Eoceno prepirenaico del Ripollés oriental. Ph.D Dissertation, Universitat Autònoma de Barcelona, Bellaterra, Barcelona, Spain.

Greene, E.A., LaMotte, A.E., Cullinan, K.A., 2005. Ground-water vulnerability to nitrate contamination at multiple thresholds in the Mid-Atlantic region using spatial probability models. U.S. Geological Survey Scientific Investigations Report 2004-5118, 24 p.

Hair JF, Anderson RE, Tatham RL, Black WC., 1998. Multivariate data analysis, 5th edition. Upper Saddle River, NJ: Pearson Education.

Happell, J.D., Opsahl , S., Top, Z., Chanton, JP., 2006. Apparent CFC and 3H/3He age differences in water from Floridian Aquifer springs. J. of Hydrology 319: 410-426.

Harbaugh, A.W., Banta, E.R., Hill, M.C., McDonald, M.G., 2000. MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model – Users guide to modularization concepts and the ground-water flow process. U.S. Geological Survey Open-File Report 00- 92, 121 p.

Harrel, F., Lee, K., Mark, D., 1996. Multivariable prognostic models: issues in developing models, evaluating assumptions and adequacy, and measuring and reducing errors. Stat Med 15: 361-387.

Harter, T., Lund, J. R., Darby, J., Fogg, G. E., Howitt, R., Jessoe, K.K., Pettygrove, G.S., Quinn, J.F., Viers, J.H., Boyle, D.B., Canada, H.E., DeLaMora, N., Dzurella, K.N., Fryjoff-Hung, A., Hollander, A.D., Honeycutt, K.L., Jenkins, M.W., Jensen, V.B., King, A.M., Kourakos, G., Liptzin, D., Lopez, E.M., Mayzelle, M.M., McNally, A., Medellin-Azuara, J., Rosenstock, T.S., 2012. Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater. Report for the State Water Resources Control Board Report to the Legislature. Center for Watershed Sciences, University of California, Davis. 78 p.

Helsel, D.R., Hirsch, R.M., 1992. Statistical Methods in Water Resources: Techniques of Water-Resources Investigations, Book 4, chapter A3. U.S. Geological Survey, 522 p.

Hershey, R.L., Mizell, S.A., Earman S., 2010. Chemical and physical characteristics of springs discharging from regional flow systems of the carbonate-rock province of the Great Basin, western United States. Hydrogeol J 18: 1007-1026.

Hipel, K.W., McLeod, AI., 1994. Time series modelling of water resources & environmental systems. Developments in water science 45. Elsevier, Amsterdam, The Netherlands 463-465.

Hiscock, K M, Lloyd, J W & Lerner, D N, 1991. Review of natural and artificial denitrification of groundwater. Wat. Res. 25 (9), 1099 - 1111.

IAEA/WMO, 2006. International Atomic Energy Agency (IAEA) in collaboration with the World Meteorological Organization (WMO). Global Network of Isotopes in Precipitation. The GNIP Database. <http://isohis.iaea.org> [last accessed 04/03/2013].

ICC (Institut Cartogràfic de Catalunya), 2011. http://www.icc.cat/eng/Home-ICC/Inici [last accessed 10/1/2011].

IDESCAT (Institut d'Estadística de Catalunya), 2012. Dades de densitat de població 2010. http://www.idescat.cat/emex/?id=24#h1 [last accessed 18/06/2012].

IDESCAT (Institut d'Estadística de Catalunya), 2013. http://www.idescat.cat [last accessed 23/04/2013].

IGC (Institut Geològic de Catalunya), unpublished. Mapa de sòls de Catalunya a escala 1:250,000, Osona (Codi ED-002/11). Generalitat de Catalunya.

IGME (Instituo Geológico y Minero de España), 2006. Mapa geológico de España, E: 1:50,000, Hoja 293, 294, 331, 332 y 364. Madrid: Instituto Geológico y Minero de España.

IGME (Instituto Geológico y Minero de España), 2009. Authors: López Geta, J.A., Fornés Azcoiti, J.M., Ramos González, G., Villarroya Gil, F. Las aguas subterráneas: un recurso natural del subsuelo. 4th Edition. Madrid.

Isaaks, E.M., Srivastava, R.M., 1989. Applied Geostatistics. Oxford University Press. New York.

Izcara, S.P, Demura K, Yamamoto Y., 2002. The nitrate pollution problem and the Agri-environmental policy in the European Union. The Review of Agricultural Economics, vol. 58, pp. 185-205.

Jalbert, J., Mathevet, T., Favre, A.C., 2011. Temporal uncertainty estimation of discharges from rating curves using a variographic analysis. J. of Hydrology 397 (1-2): 83-92.

Johnson, T.D., Belitz, K., 2009. Assigning land use to supply wells for the statistical characterization of regional groundwater quality: correlating urban land use and VOC occurrence. Journal of Hydrology 370, 100-108.

Jones, A.L., Smart, P.L., 2005. Spatial and temporal changes in the structure of groundwater nitrate concentration time series (1935-1999) as demonstrated by autoregressive modelling. J. of Hydrology 310: 201-215.

Katz, B.G., Böhlke, J.K., Hornsby, H.D., 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. Chem Geol 179: 167-186.

Katz, B.G., Chelette, A.R., Pratt, T.R., 2004. Use of chemical and isotopic tracers to assess nitrate contamination and ground-water age, Woodville Karst Plain, USA. J. of Hydrology 289: 36-61.

Katz, B.G., Hornsby, H.D., Böhlke, J.K., Mokray, M.F., 1999. Sources and chronology of nitrate contamination in spring waters, Suwannee River Basin, Florida. U.S. Geological Survey Water-Resources Investigations Report; p. 99-4252.

Katz, B.G., Sepulveda, A.A., Verdi, R.J., 2009. Estimating nitrogen loading to ground water and assessing vulnerability to nitrate contamination in a large karstic springs basin, Florida. J. Am. Water Resour. As. 45: 607–627.

Katz, B.G., 2004. Sources of nitrate contamination and age of water in large karstic springs of Florida. Environmental Geology 46: 689-706.

Kendall, C., 1998. Chapter 16: Tracing nitrogen sources and cycles in catchments, p. 519-576, in: Kendall C, JJ McDonnell. Isotope tracers in catchment hydrology. Elsevier Science BV. Amsterdam, The Netherlands, 839 p.

Kitanidis, P.K., 1997. Introduction to Geostatistics: Applications in Hydrogeology. Cambridge University Press, Cambridge, United Kingdom.

Kleinbaum, D.G., 1994. Logistic regression, a self-learning text: New York, Springer-Verlag, 282 p.

Kresic, N., Stevanovic, Z., 2010. Groundwater hydrology of springs. Engineering, theory, management, and sustainability. Jordan Hill, Oxford: Butterworth-Heinemann, Elsevier.

Leibundgut, C., 1998. Tracer-based assessment of vulnerability in mountainous headwaters. In: Kovar K, Tappeiner U, Peters NE, Craig RG, editors. Hydrology, Water Resources mid Ecology in Headwaters (Proceedings of the HeadWater'98, Merano, Italy). IAHS Publ. 248: 317-325.

Liggett, J.E., Talwar, S., 2009. Groundwater Vulnerability Assessments and Integrated Water Resource Management, Streamline Watershed Management. Vol. 13/no.1 Bulletin Fall 2009, article 4, pp. 18-29.

Lindsey, B.D., Falls, W.F., Ferrari, M.J., Zimmerman, T.M., Harned, D.A., Sadorf, E.M., Chapman, M.J., 2006. Factors affecting occurrence and distribution of selected contaminants in ground water from selected areas in the Piedmont Aquifer System, eastern United States, 1993-2003. U.S. Geological Survey Scientific Investigations Report 2006-5104.

Liu, A., Ming, J., Ankuman, R.O., 2005. Nitrate contamination in private wells in rural Alabama, United States. Science of the Total Environment 346: 112-120.

Manga, M., 2001. Using springs to study groundwater flow and active geologic processes. Annu. Rev. of Earth Pl. Sc. 29, 201-228.

Mas-Pla, J., Menció, A., Brusi, D., Soler, A., Puig, R., Palau, J., Montaner, J., Pons, P., López, J., 2008. Estudi hidrogeològic i multiisotòpic del Lluçanès: definició de recursos i àrees de protecció. Unpublished results. Technical report funded by ACA and CCO.

Mas-Pla, J., Menció, A., Soler, A., Otero, N., 2006. Avaluació de la contaminació per nitrat de les aigües subterrànies a la Plana de Vic: Estudi de la dinámica hidrogeològica i anàlisi multiisotòpica. Unpublished results. Technical report funded by ACA, CCO and ASSAPORC.

Matschullat, J., Ottenstein, R., Reimann C., 2000. Geochemical background – can we calculate it? Environ Geol 39(9): 990-1000.

Meinzer, O.E., 1923. The occurrence of ground water in the United States with a discussion of principles. U.S. Geological Survey Water-Supply Paper 489, Washington, DC.

Menard, S.W., 2001. Applied Logistic Regression Analysis, 2nd Ed. Sage University Papers Series on Quantitative applications in the Social Sciences, 07-106. Thousand Oaks, CA: Sage.

Menció, A., Boy, M., Mas-Pla, J., 2011a. Analysis of vulnerability factors that control nitrate occurrence in natural springs (Osona region, NE Spain). Journal of Science of the Total Environment 409, 3049-3058.

Menció, A., Mas-Pla, J., Otero, N., Soler, A., 2011b. Nitrate as a tracer of groundwater flow in a fractured multilayered aquifer. Hydrological Sciences Journal, 56:1, 108-122.

MMA (Ministerio de Medio Ambiente), 2000. Libro blanco del Agua en España. Secretaría de Estado de Aguas y Costas. Madrid: 1 – 637 pp.

Molinero, J., Custodio, E., Sahuquillo, A., Llamas, M.R., 2011. Groundwater in Spain: legal framework and management issues. A: "Groundwater management practices". CRC Press/Balkema, p. 123-137.

Moncaster, S.J., Bottrell, S.H., Tellam, J.H., Lloyd, J.W., Konhauser, K.O., 2000. Migration and attenuation of agrochemical pollutants: insights from isotopic analysis of groundwater sulphate. J. of Contaminant Hydrology 43, 147-163.

Mueller, D.K., and Helsel, D.R., 1996. Nutrients in the Nation's waters: Too much of a good thing? U.S. Geological Survey Circular 1136, 24 p.

Nolan, B.T., 2001. Relating nitrogen sources and aquifer susceptibility to nitrate in shallow ground water of the United States. Ground Water 39, 2, 290-299.

Nolan, B.T., Hitt, K.J., 2006. Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. Environmental Science and Technology 40, 24, 7834-7840.

Nolan, B.T., Hitt, K.J., Ruddy, B.C., 2002. Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. Environmental Science and Technology 36, 10, 2138–2145.

Nowlan, L., 2005. Buried treasure: Groundwater permitting and pricing in Canada. Walter and Duncan Gordon Foundation, with case studies by Geological Survey of Canada, West Coast Environmental Law, and Sierra Legal Defence Fund.

Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J., 2009. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain). Agriculture, Ecosystems and Environment 133, 103-113.

Panno, S.V., Hacley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. Chemical Geology 179: 113-128.

Panno, S.V., Kelly, W.R., Martinsek, A.T., Hackley, K.C., 2006. Estimating background and threshold nitrate concentrations using probability graphs. Ground Water 44(5): 697-709.

Panno, S.V., Kelly, W.R., 2004. Nitrate and herbicide loading in two groundwater basins of Illinois' sinkhole plain. J. of Hydrology 290:229-242.

Pauwels, H., Foucher, J.C., Kloppmann, W., 2000. Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. Chemical Geology 168, 307-324.

Perrin, J., Jeannin, P.Y., Cornaton, F., 2006. The role of tributary mixing in chemical variations at a karst spring, Milandre, Switzerland. J. of Hydrology 332:158-173.

Peterson, E.W., Davis, R.K., Brahana, J.V., Orndorff, H.A., 2002. Movement of nitrate through regolith covered karst teranne, northwest Arkansas. J. of Hydrology 256: 35-47.

Prat, F., 1999. Qualitat de les aigües subterrànies de la comarca d'Osona. Col·legi Oficial de Farmacèutics de la província de Barcelona – Universitat de Barcelona.

Price, C.V., Nakagaki, N., Hitt, K. J., 2010. National Water-Quality Assessment (NAWQA) Area-Characterization Toolbox, Release 1.0: U.S. Geological Survey Open-File Report 2010-1268 (online-only).

Reguant, S., 1967. El Eoceno marino de Vic (Barcelona). Mem Inst Geol Min Esp 67: 330 pp.

Rein, A., Hoffmann, R., Dietrich, P., 2004. Influence of natural time-dependent variations of electrical conductivity on DC resistivity measurements. J. of Hydrology 285: 215-232.

Rowden, R.D., Liu, H., Libra, R.D., 2001. Results from the Big Spring basin water quality monitoring and demonstration projects, Iowa, EUA. Hydrogeology J. 9: 487-497.

Rupert, M.G., 2003. Probability of detecting atrazine/desethyl-atrazine and elevated concentrations of nitrate in ground water in Colorado. U.S. Geological Survey Water-Resources Investigations Report 02-4269.

Salgado, M.J., Pérez-López, M., Alonso, J., García, M.A., Melgar, M.J., 2003. Assessment of drinking water contamination at springs along the road to Santiago (NW Spain). J. Environ Sci Heal, Vol A38, No. 4, 609-617.

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Schilling, K.E., Zhang, Y.K., Hill, D.R., Jones, C.S., Wolter, C.F., 2009. Temporal variations of *Escherichia coli* concentrations in a large Midwestern river. J. of Hydrology 365: 79 - 85.

Shiklomanov, I.A., Rodda, J.C., 2003. World Water Resources at the beginning of the Twenty-First Century. Cambridge University Press, New York.

SMC (Servei Meteorològic de Catalunya), 2012. Xarxa agrometeorològica de Catalunya. http://www.ruralcat.net/web/guest/agrometeo.estacions [last accessed 13/06/2012].

Spalding, R.F., Exner, M.E., 1993. Occurrence of nitrate in ground-water—a review. J Environ Qual. 22:392–402.

Stackelberg, P.E., Barbash, J.E., Gilliom, R.J., Stone, W.W., Wolock, D.M., 2012. Regression models for estimating concentrations of atrazine plus deethylatrazine in shallow groundwater in agricultural areas of the United States. Journal Environmental Quality 41.

Stackelberg, P.E., Gilliom, R.J., Wolock, D.M., Hitt, K.J., 2006. Development and application of a regression equation for estimating the occurrence of atrazine in shallow ground water beneath agricultural areas of the United States: U.S. Geological Survey Scientific Investigations Report 2005-5287, 12 p., online only.

Steichen, J., Koelliker, J., Grosh, D., Heiman, A., Yearout, R., Robbins, V., 1988. Contamination of farmstead wells by pesticides, volatile organics, and inorganic chemicals in Kansas. Ground Water Monitoring Review 8, 153-160.

Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley and Sons, New York.

Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., 2011. The European Nitrogen Assessment: sources, effects and policy perspectives. Cambridge University Press, New York. 664 p.

Tesoriero, A.J., Voss, F.D., 1997. Predicting the probability of elevated nitrate concentrations in the Puget Sound Basin: implications for aquifer susceptibility and vulnerability. Ground Water 35, 1023–1039.

Torrentó, C., 2010. Denitrification with pyrite for bioremediation of nitrate contaminated groundwater. PhD dissertation. University of Barcelona; 285 pp.

Torrentó, C., Urmeneta, J., Otero, N., Soler, A., Viñas, M., Cama, J., 2011. Enhanced denitrification in groundwater and sediments from nitrate-contaminated aquifer after addition of pyrite. Chemical Geology 287: 90-101.

Toth, D.J., Katz, B.G., 2006. Mixing of shallow and deep groundwater as indicated by the chemistry and age of karstic springs. Hydrogeol J 14: 1060-1080.

Van Grinsven, H.J., Ward, M.H., Benjamin, N., de Kok, T.M., 2006. Does the evidence about health risks associated with nitrate ingestion warrant an increase of the nitrate standard for drinking water? Environmental Health: A Global Access Science Source 2006, 5, 26.

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

Vitòria, L., 2004. Estudi multi-isotòpic ($\delta^{15}N$, $\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$, δD i $^{87}Sr/^{86}Sr$) de les aigües subterrànies contaminades per nitrats d'origen agrícola i ramader. Translated title: Multi-isotopic study ($\delta^{15}N$, $\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$, δD i $^{87}Sr/^{86}Sr$) of nitrate polluted groundwater from agricultural and livestock sources. PhD dissertation. University of Barcelona; 188 pp.

Vitòria, L., Soler, A., Canals, A., Otero, N., 2008. Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: example of Osona (NE Spain). Applied Geochemistry 23, 3597-3611.

Volkmer, B.G., Ernst, B., Simon, J., Kuefer, R., Bartsch, G. Jr., Bach, D., Gschwend, J.E., 2005. Influence of nitrate levels in drinking water on urological malignancies: a community-based cohort study. Br. J. Urol. Int. 95: 972–976.

Vrba, J., Zaporozec, A., 1994. Guidebook on Mapping Groundwater Vulnerability. Volume 16. Heise. International Association of Hydrogeologists. Hannover.

Ward, M.H., Brender, J.D., 2011. Drinking water nitrate and health, In: Editor-in-Chief: Jerome O. Nriagu, Editor(s)-in-Chief, Encyclopedia of Environmental Health, Elsevier, Burlington, pp. 167-178.

Ward, M.H., deKok, T.M., Levallois, P., Brender, J., Gulis, G., Nolan, B.T., VanDerslice, J., 2005. Workgroup report: drinking-water nitrate and health—recent findings and research needs. Environ. Health Perspect. 113, pp. 1607–1614.

WHO (World Health Organization), 2011a. *Guidelines for Drinking-water Quality*. *4th Ed.* Chapter 8: Chemical aspects and Chapter 12: Chemical fact sheets. Geneva, Switzerland.

WHO (World Health Organization), 2011b. Nitrate and nitrite in drinking-water: background document for development of WHO *Guidelines for Drinking-water Quality*. Geneva, Switzerland.

WHO, 2008. Guidelines for drinking-water quality. 3rd Edition. Geneva, World Health Organization.

Wilcox, J.D., Bradbury, K.R., Thomas, C.L., Bahr, J.M., 2005. Assessing background ground water chemistry beneath a new unsewered subdivision. Ground Water 43: 787-795.

Worral, F., Burt, T.P., 1999. A univariate model of river water nitrate time series. J. of Hydrology 214: 74-90.

WWAP (World Water Assessment Programme, 2006. Water a shared responsibility. The United Nations World Water Development Report 2. UNESCO, Paris, France.

Zaporezec, A., 2002. Groundwater contamination inventory: a methodological guide. IHP-VI, Series on Groundwater No.2, UNESCO.

Zhang, Y.K., Schilling, K., 2005. Temporal Variations and Scaling of Streamflow and Baseflow and their Nitrate-Nitrogen Concentrations and Loads. Adv. in Water Resources 28: 701-719.