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

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HIGHLIGHTS

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

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ABSTRACT

Non-point agricultural pollution is a major concern in groundwater management. To investigate nitrate input to the subsurface through groundwater recharge, thirteen natural springs were sampled. Discharge, electrical conductivity (EC), nitrate concentration, pH value and water temperature were monitored every two weeks from January 2010 till February 2011 at selected springs in the Osona region (NE Spain). Two extensive hydrochemical analyses were also conducted at the beginning and at the end of the survey. Springs are classified in four groups describing their hydrological response, based on discharge, EC and nitrate data. Geostatistical analysis provides an additional insight into the discharge and nitrate temporal pattern.

Even though discharge and EC can be related to specific hydrogeological behaviours, nitrate content shows uniform values in most of the springs with only a minor influence from external factors such as rainfall events, fertilisation regimes and geological traits. Such evenness of outflow might be attributed to a homogenisation of the subsurface processes that determine nitrate infiltration after decades of intensive fertilisation using pig manure. Accumulated nitrate mass load and variograms confirm this result. Assuming that spring data are representative of nitrate leaching towards the underlying aquifer, nitrate content of infiltrating recharge in shallow aquifers should therefore show a steady value over time with only small fluctuations due to natural processes. Nevertheless, temporal fluctuations in nitrate content in aquifers could be also attributed to flow regime alterations due to human groundwater withdrawal.

1. Introduction

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

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

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

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

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

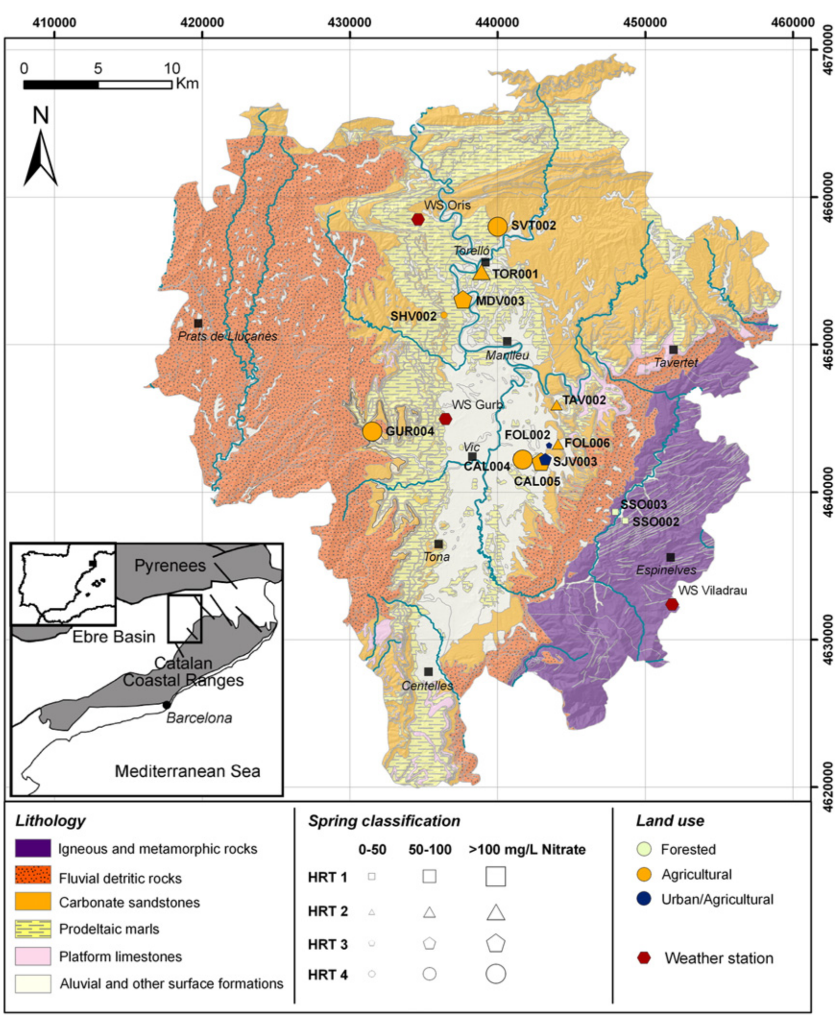

Fig. 1. Map of the geographical and geological setting of springs and the study area, with the locations and characteristics of the springs. Hydrological Response Types (HRT) are described later in Section 4.2. Geological formations are mapped according to the main lithology in the area (geological cartography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

1999) and therefore to investigate hydrological processes that occur in the subsurface (Rein et al., 2004; Wilcox et al., 2005). Variogram analysis is one of the most common measure of spatial variability. However, it has also been used to characterise temporal data sets. For instance, Zhang and Schilling (2005) used variograms to analyse the patterns of temporal variations of precipitation, streamflow and baseflow, as well as their nitrate concentrations and loads from a long-term record of 28 years. Aubert et al. (2012) studied the inter-annual variability of nitrate, sulphate, chloride and dissolved organic and inorganic carbon of stream water and groundwater using variograms.

Regarding nitrate variability in groundwater in the Osona region, Menció et al. (2011a) found that, after a monthly survey of a set of 85 wells during a year, 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 characterise the hydrologic and hydrochemical responses of springs to rainfall regimes and land uses, with special emphasis on nitrate concentrations, as a means to understand nitrate recharge rates to aquifers (Fig. 2). Common and/or distinctive patterns among springs, based on their geological setting and hydrologic behaviour, are sought in order to explain the migration of nitrogen from its application as fertiliser on the soil to its occurrence as nitrate in springs and eventually in groundwater. These patterns are named Hydrologic Response Types (HRT). In this study, we use variograms with the aim to objectively compare different temporal trends, and to describe how temporal continuity changes as a function of time lags.

2. Geological and hydrogeological setting

2.1. Regional geology and hydrogeology

The Osona region is an area rich in natural springs due to its geological and geomorphological characteristics. The geological system consists of a sequence of Paleogene sedimentary layers, with a total thickness of approximately 1500 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) (Fig. 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.

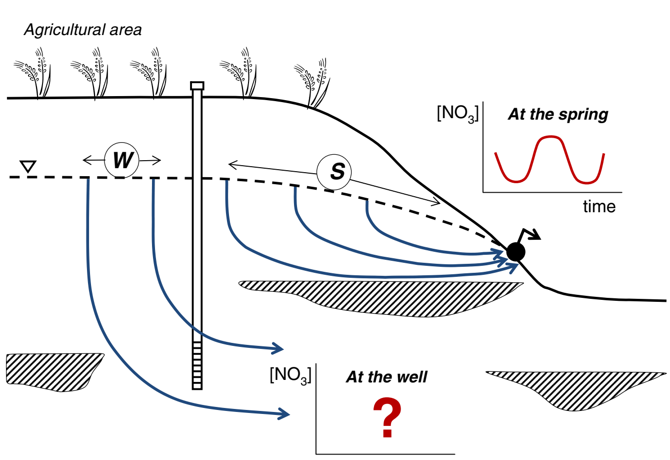

Fig. 2. Conceptual scheme of subsurface flow feeding a spring and the aquifer in a similar geological setting. Geological features, such as clay lenses (cross-hatched), account for the aquifer heterogeneity and determine the position and occurrence of the spring. Recharge areas feeding the spring and the well are referred to as S and W, respectively, in the scheme. The cross-section is not to scale.

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.

2.2. Spring characterisation

Springs are categorised according to different variables which help to explain their different hydrological behaviours. 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 (Figs. 1 and 3, Table 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 maximise 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 (Fig. 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 L per second (Table 1).

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; Fig. 1), the annual mean temperature is 12.6 °C; and mean precipitation and potential evapotranspiration (using the Thornthwaite equation) are around 715 and 706 mm/

Fig. 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).

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 Figs. 4 to 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. 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 programme 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.

3.1. 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

Table 1
Spring typology and basic statistics for the physicochemical parameters of spring water samples over the 27 campaigns.

HRT	Spring code	Spring name	n	Discharge (L/s)		EC (uS/cm)		NO_3^- (mg/L)		Total NO_3^- mass load (kg)	pH		Water temp. (°C)		Geological type	Land use
				ME	SD	ME	SD	ME	SD		ME	SD	ME	SD		
1	SSO002	Font del Rifà	26[a]	0.162	0.03	407.4	34.4	10.3	1.0	56	7.0	0.1	12.7	0.6	A	Forested
	SSO003	Font dels Peons	26[a]	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	Font 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	Font 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	Font dels Ocells	26[a]	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	Font de l'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	Font 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	Font del Peretó	27	0.701	0.33	1080	71.9	222.1	19.6	5447	7.0	0.1	14.0	0.7	C	Agricultural
	SJV003	Font d'en Titus	26[b]	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	Font de la Gana	27	0.542	0.65	1134.2	91.3	280.6	83.1	6129	7.0	0.1	13.2	0.9	C	Agricultural
	GUR004	Font Salada	27[c]	0.107	0.08	1343.3	75.6	390.9	26.1	1425	7.1	0.2	13.2	0.5	B	Agricultural
	SHV002	Font 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	Font de 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.
Geological type: A: crystalline rocks; B: pre-quaternary sedimentary rocks; C: quaternary sediments.
[a] Nitrate concentration from one campaign (July'10) was not used in the statistics because of analytical error.
[b] 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).
[c] 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.

were periodically analysed to check for any differences between stream and spring water. Two extensive hydrochemical analyses, 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 metre with a temperature measurement capability (accuracy EC ≤ 0.5%; temperature ≤ 0.2 °C). pH was also measured in situ with a WTW-330i pH metre (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 4 °C before being analysed. Nitrate and nitrite contents were analysed by ion-exchange chromatography while ammonium was analysed 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 analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). Geochemical modelling (PRHREEQC) was used to calculate carbon dioxide partial pressure (P_{CO_2}) and the calcite saturation index.

3.2. Exploratory statistics and geostatistical analyses

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 categorised on the basis of the variability 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 Figs. 4 to 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 behaviours (Section 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 normalised 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. This analysis lays on the experimental semi-variogram (hereafter simply 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). An estimate of the experimental variogram is given by:

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

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 discharge and nitrate. In those cases where the correlation coefficient between the reference and the drift functions was higher than 0.5, data was detrended using ordinary least squares. This was done 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.

4. Results

4.1. Hydrochemistry of the springs

Mean nitrate concentration in springs ranged from 8 to 391 mg/L (Table 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.

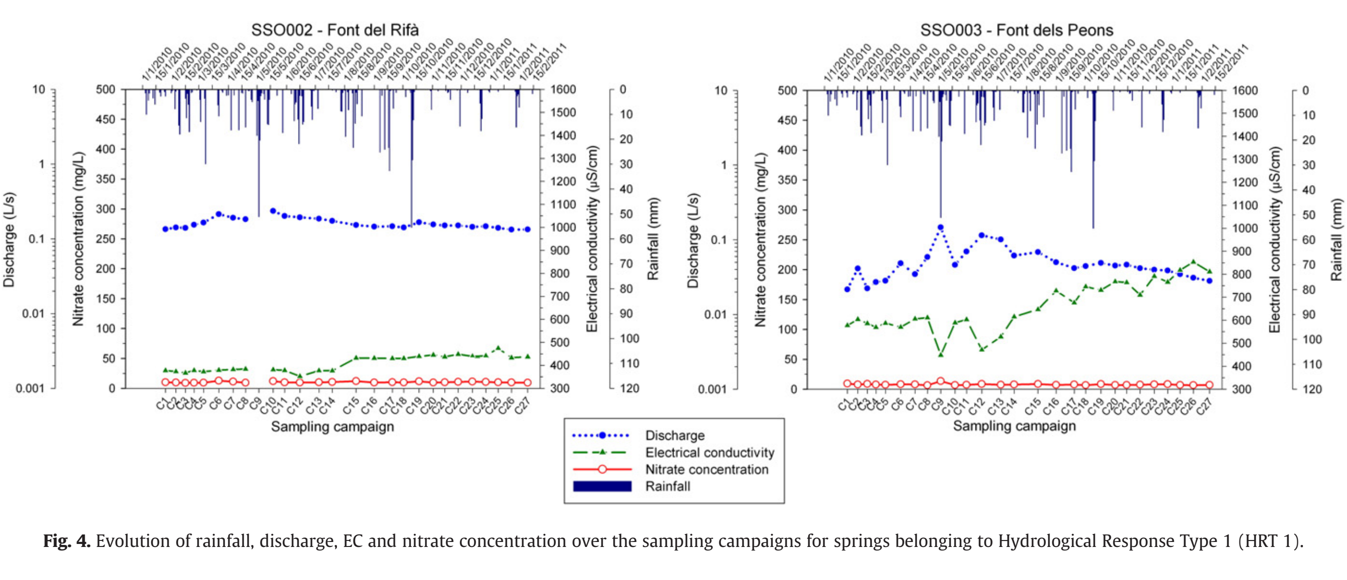

Fig. 4. Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 1 (HRT 1).

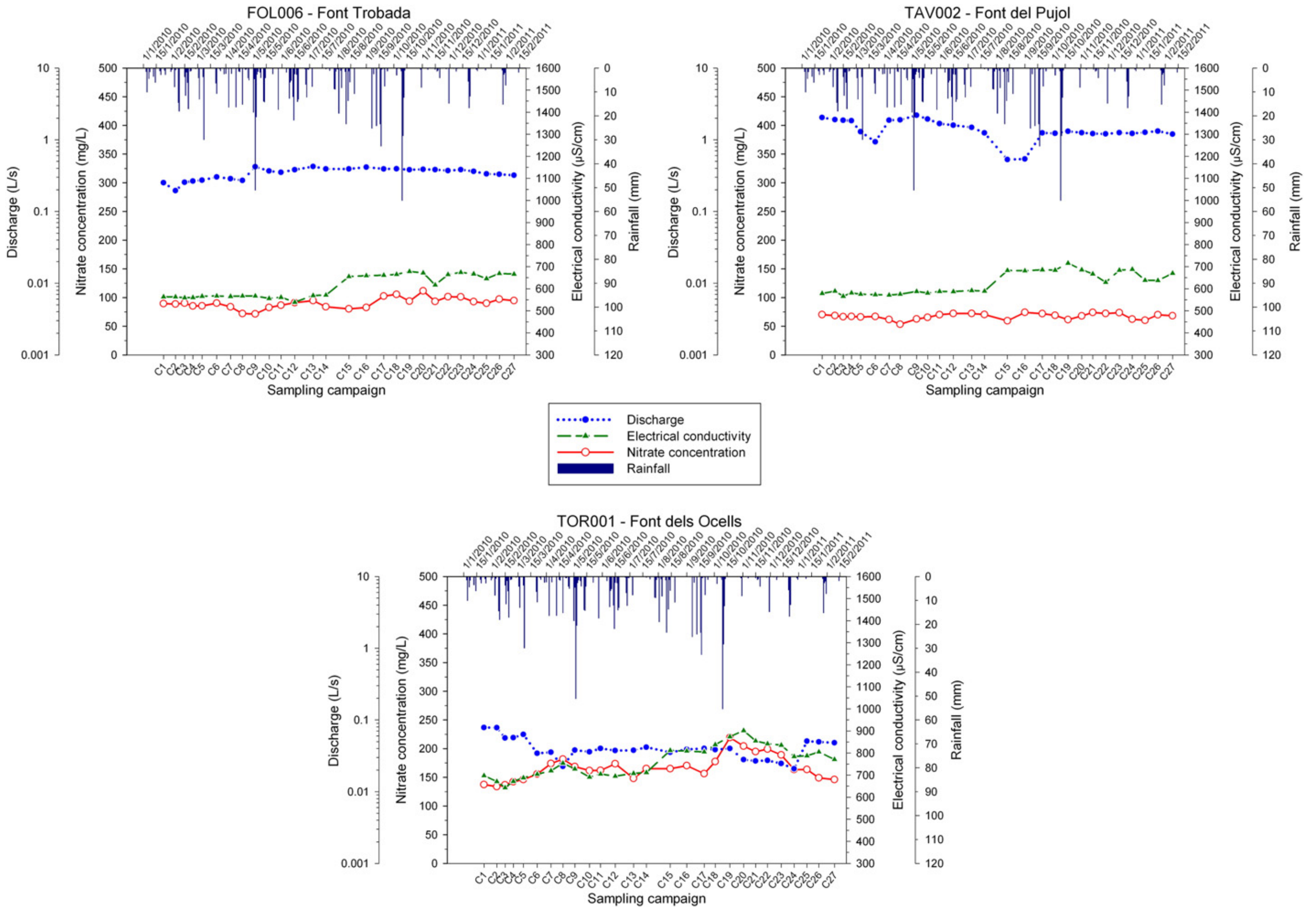

Fig. 5. Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 2 (HRT 2).

Electrical conductivities varied from 407 µS/cm at the most pristine spring, to 1343 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 the Plana de Vic, which is associated with the occurrence of carbonate sandstone formation (e.g. FOL002, FOL006 and TAV002; Fig. 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 (Section 5).

Mean pH values varied between 6.9 and 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 14.3 °C.

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 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, SO_4^{2-} did not show any particular correlation with nitrate ($r^2 = 0.49$). 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).

4.2. Discharge, electrical conductivity and nitrate time series

For ease of reference, the characteristics of the different Hydrological Response Type groups are summarised in Table 3. Figs. 4 to 7 represent the time trends of spring discharge, EC and nitrate content, and average daily rainfall data from the Osona region. pH values and water temperature are not shown as they were constant throughout the year.

The features of each Hydrological Response Type (HRT) shown in the graphs in Figs. 4 to 7 are as follows:

- *Hydrological Response Type 1* (*HRT 1*); Fig. 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 fertiliser 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.
- *Hydrological Response Type 2* (*HRT 2*); Fig. 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 1). These springs drain widespread surface

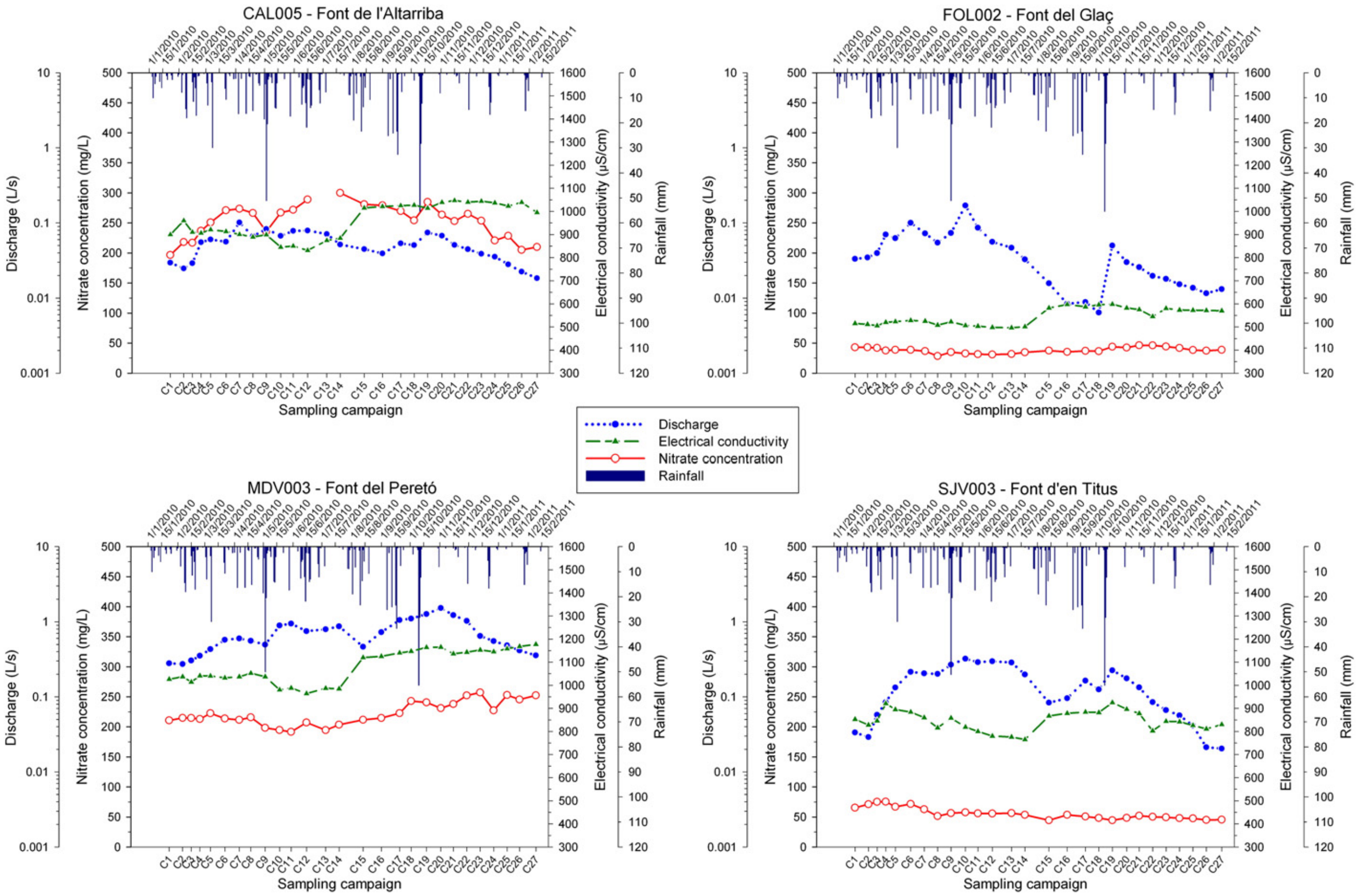

Fig. 6. Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 3 (HRT 3).

deposits (alluvial, colluvial and eluvial), usually with large hydraulic conductivity values (group C). They are characterised by a relatively uniform discharge, EC and nitrate content over time with little influence from rainfall.

- *Hydrological Response Type 3* (*HRT 3*); Fig. 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.
- *Hydrological Response Type 4* (*HRT 4*); Fig. 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.

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 1, and the normalised mass evolution for each spring, grouped according to its HRT, is plotted in Fig. 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 (Figs. 4 and 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.

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

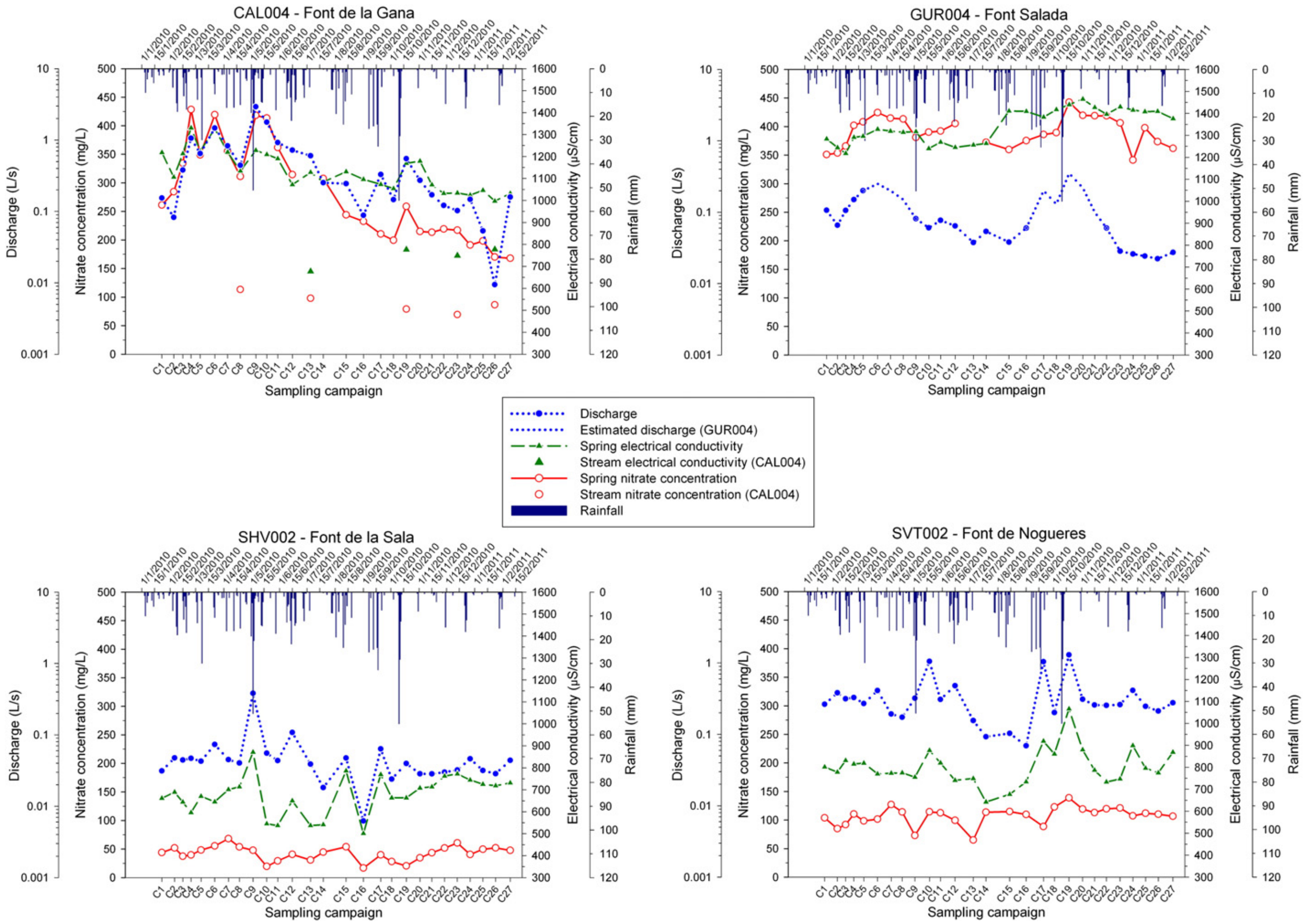

Fig. 7. Evolution of rainfall, discharge, EC and nitrate concentration over the sampling campaigns for springs belonging to Hydrological Response Type 4 (HRT 4). EC and nitrate data for the stream located near CAL004 are also shown. Estimated discharge, based on field observations, for non-gauged months at GUR004 is indicated by a broken line without symbols.

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 Fig. 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.

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 (Figs. 9 and 10). Variogram model parameters for discharge and nitrate are presented in Table 4.

4.4.1. Discharge variograms

The discharge variograms reflect the flow patterns of each of the hydrological response types (Fig. 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 characterised 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 characterised 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.

4.4.2. Nitrate variograms

Nitrate variograms for the HRT1 springs show a uniform variability for any lag time (Fig. 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

Table 2
Hydrochemical results of the sampling campaigns of February 2010 and February 2011.

HRT	Spring code	EC (μS/cm)	pH	Water T(°C)	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	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	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	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%.

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 characterised 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 homogenised 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 modelled 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 behaviour with similar ranges of 3.5–4.5 months (6.5–8.5 sampling campaigns).

Finally, HRT4 springs are characterised 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 (Figs. 7 and 8), is evidenced by the small range of the modelled variograms. Again, the relationship between stream leakage and spring behaviour 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.

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

Table 3
Main features of each variable within each Hydrological Response Type (HRT).

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

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

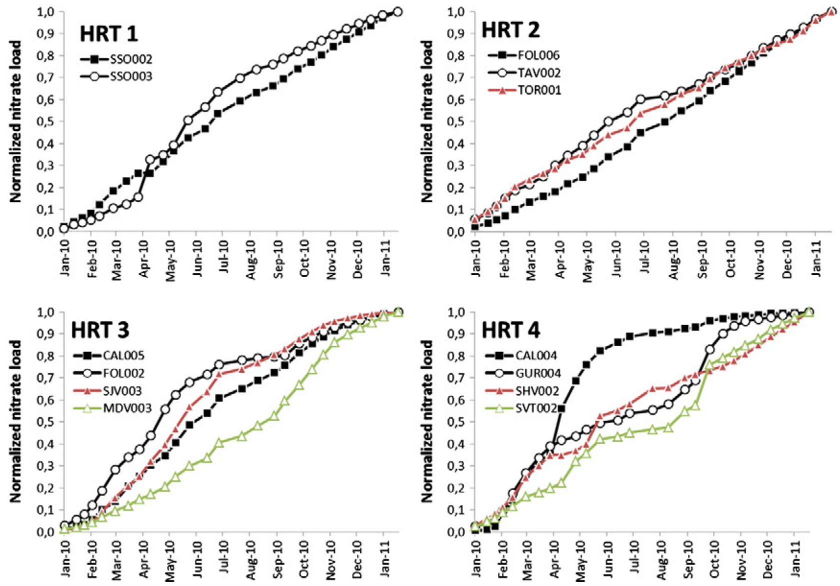

Fig. 8. Normalised nitrate accumulated mass load for each HRT.

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

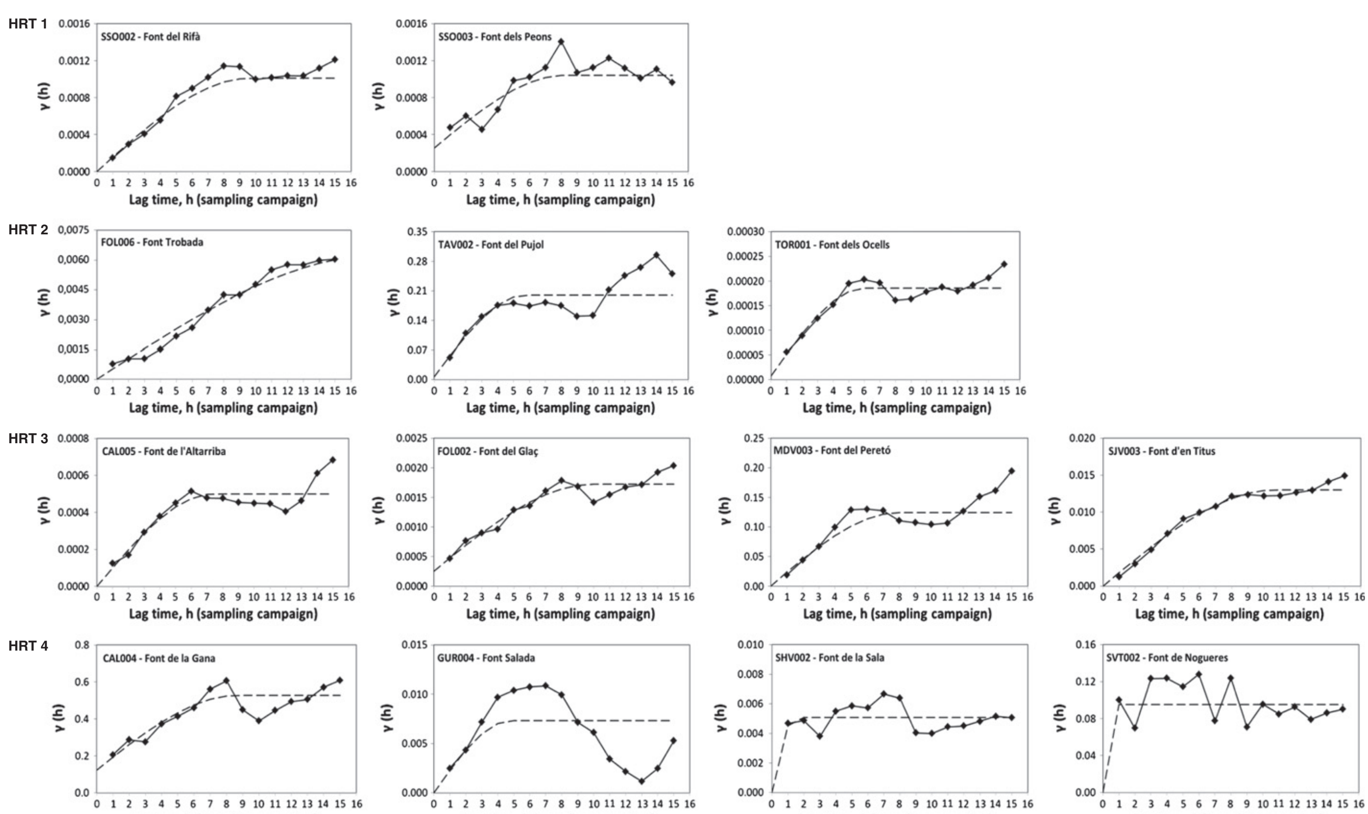

Fig. 9. Experimental and fitted variograms for discharge data. The solid line represents the experimental variogram and the dashed line is the model variogram.

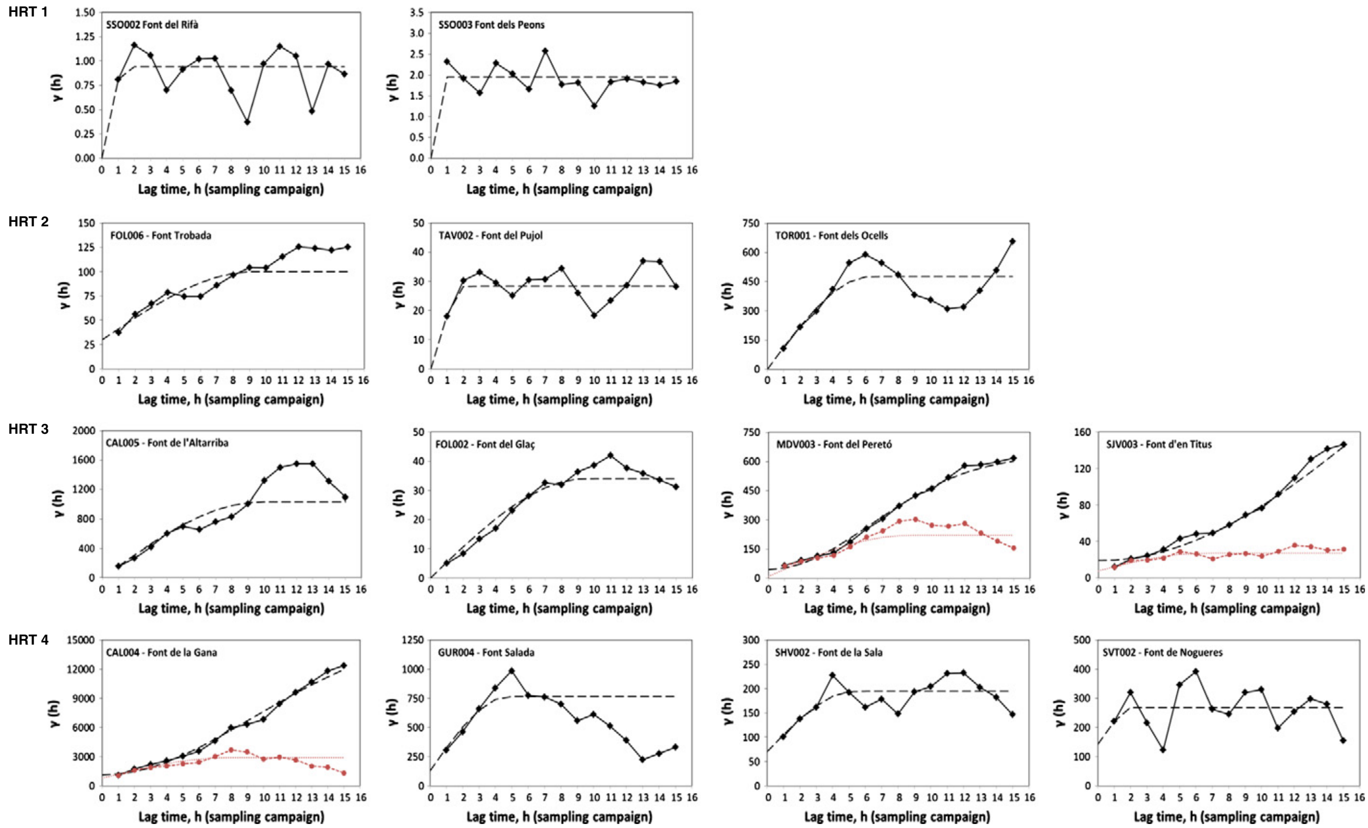

Fig. 10. Experimental and fitted variograms for nitrate data. The solid line represents the experimental variogram and the dashed line is the model variogram. The red and dotted line represents the experimental and model variogram for detrended data.

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 (Figs. 4 to 7), no significant changes in nitrate content related to rainfall events or fertilisation regimes over the sampling period

Table 4
Basic statistics of the discharge and nitrate data and variogram model parameters.

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.

were observed. This observation points to a homogenisation of the nitrate concentration in the subsurface from the spring recharge areas, where crop fertilisation 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 behaviours distinguished in this research, summarised 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 homogenised 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 behaviour. 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 behaviours 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 fertilisation, 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 homogenisation 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 (Figs. 4 to 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 behaviour). 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. Flowlines that recharge groundwater resources at depth, instead of outcropping to the surface through springs, might then follow a similar behaviour. We can thus expect a constant nitrate concentration in shallow aquifers after years of fertilisation practices where flow fields have not been largely disturbed by groundwater withdrawal.

6. Conclusions

Four different types of hydrological responses (HRT) are identified in the Osona region based on geology, discharge regime, electrical conductivity and nitrate content variations. In particular, discharge and electrical conductivity show a consistent behaviour that determines the specific hydrogeological dynamics for each HRT. However, nitrate records generally appear uniform over time. Geostatistical analyses also support the finding that nitrate content in most of the springs is constant with small variability patterns. Moreover, most accumulated normalised-nitrate mass load plots show a progressive increase in most springs over the 27 campaigns, only modified by large alterations to the flow system due to major rainfall events. Such a constant increment is evidence of a fairly stable subsurface nitrate mass flow towards the springs, and therefore to groundwater recharge.

The findings of this research suggest that land uses and agricultural practices, especially the amount of fertiliser applied over several decades, finally determines the magnitude of nitrate content in groundwater, although its natural variability remains small. Ultimately, geochemical processes in the subsurface, such as mixing and/or denitrification, 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 a valid measure 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.

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