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Corresponding Author: Dr. Anna Menció, Ph.D.

Corresponding Author's Institution: Universitat de Girona

First Author: Anna Menció, Ph.D.

Order of Authors: Anna Menció, Ph.D.; Josep Mas-Pla, Ph.D; Neus Otero, Ph.D; Oriol Regàs, M.D.; Mercè Boy-Roura, Ph.D; Roger Puig, Ph.D; Joan Bach, Ph.D; Cristina Domenech, Ph.D; Albert Folch, Ph.D

Abstract: Contamination from agricultural sources and, in particular, nitrate pollution, is one of the main concerns in groundwater management. However, this type of pollution entails the entrance of other substances into the aquifer, as well as it may promote other processes. In this study, we deal with hydrochemical and isotopic analysis of groundwater samples from four distinct zones in Catalonia (NE Spain), which include different lithological units, to investigate the influence of manure fertilization on the overall hydrochemical composition of groundwater. Results indicate that high nitrate concentrations, resulting from intense manure application, homogenize the contents of the major dissolved ions (i.e.; Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>). Moreover, positive linear relationships between nitrate and some ions are found indicating the magnitude of the fertilization impact on groundwater hydrochemistry. Nevertheless, the increasing concentration of specific ions is not only attributed to the manure input, but to the enhancing effect of manure and slurry upon the biogeochemical processes that control water-rock interactions. Such results raise awareness that such processes should be evaluated in advance in order to assess adequate groundwater resources assessment.

Suggested Reviewers: Bernard T Nolan Ph.D

U.S Geological Survey

btnolan@usgs.gov

Dr. B.T. Nolan is an expert on nitrate pollution, and the different methods used to determine nitrate occurrence and distribution (such as logistic regression).

Elisa Sacchi Ph.D

Università degli Studi di Pavia

elisa.sacchi@unipv.it

Dr. E. Sacchi has a wide experience as in environmental geochemistry, and especially, the environmental application of isotopes geochemistry.

Thomas Harter Ph.D

University of California

thharter@ucdavis.edu

Dr. T. Harter is an expert on hydrogeology, especially on groundwater pollution transport.

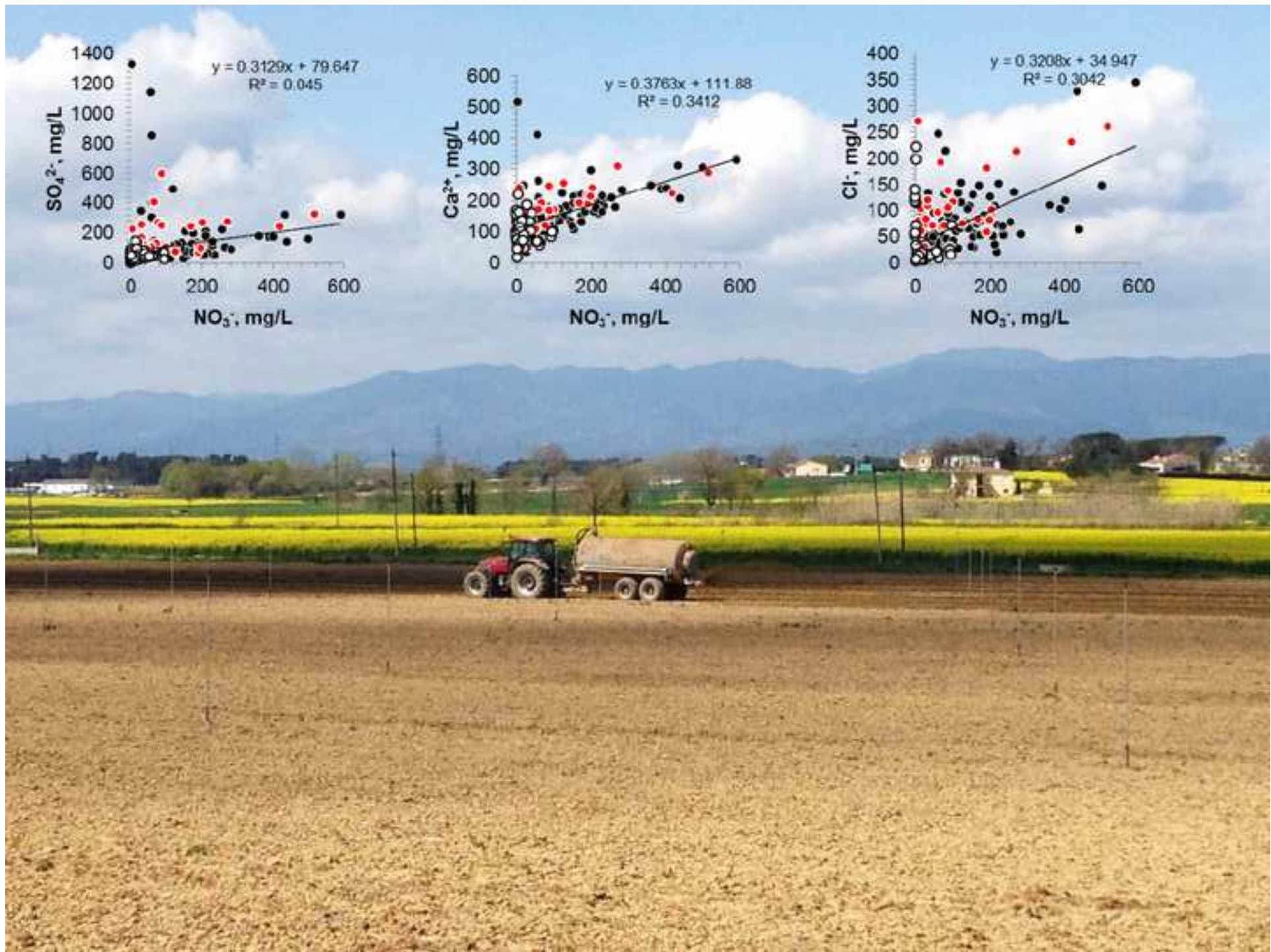
Corinne Le Gal La Salle  
Université de Nîmes  
corinne.legallasalle@unimes.fr

Dr. C. Le Gal La Salle has a wide experience in geochemistry and isotopic characterization of natural and polluted waters.

Albert Soler Ph.D  
Universitat de Barcelona  
albertsolergil@ub.edu

Dr. A. Soler is an expert on nitrate pollution, and especially on the use of nitrate isotopes.

Opposed Reviewers:



## Highlights

- The effects of nitrate pollution have been evaluated in five different aquifer types
- Statistical and multivariate analyses are used to identify groundwater changes
- Agricultural pollution modifies groundwater conditions and geochemical processes

# Nitrate pollution of groundwater; all right..., but nothing else?

Anna Menció<sup>1</sup>, Josep Mas-Pla<sup>1,2</sup>, Neus Otero<sup>3</sup>, Oriol Regàs<sup>1</sup>, Mercè Boy-Roura<sup>2</sup>, Roger Puig<sup>3</sup>, Joan Bach<sup>5</sup>, and Cristina Domenech<sup>3</sup>, Albert Folch<sup>5</sup>

<sup>1</sup> Grup de Geologia Aplicada i Ambiental (GAiA), Centre de Recerca en Geologia i Cartografia Ambiental (Geocamb), Dept. de Ciències Ambientals, Universitat de Girona, Spain, e-mail: [anna.mencio@udg.edu](mailto:anna.mencio@udg.edu)

<sup>2</sup> Institut Català de Recerca de l'Aigua (ICRA), Spain, email: [jmas@icra.cat](mailto:jmas@icra.cat).

<sup>3</sup> Grup de Mineralogia Aplicada i Geoquímica de Fluids, Dept. de Cristal·lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Spain, email: [notero@ub.edu](mailto:notero@ub.edu).

<sup>4</sup> Àrea de Geodinàmica Externa i Hidrogeologia, Dept. de Geologia, Universitat Autònoma de Barcelona, Bellaterra, Spain, email: [joan.bach@uab.cat](mailto:joan.bach@uab.cat).

<sup>5</sup> Grup d'Hidrologia Subterrània, Dept. D'Enginyeria del Terreny, Cartogràfica i Geofísica. Universitat Politècnica de Catalunya-Barcelona Tech, Spain, email: [folch.hydro@gmail.com](mailto:folch.hydro@gmail.com).

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**KEY WORDS:** nitrate pollution, hydrochemistry, water-rock interaction, multivariate analysis, groundwater

## ABSTRACT

Contamination from agricultural sources and, in particular, nitrate pollution, is one of the main concerns in groundwater management. However, this type of pollution entails the entrance of other substances into the aquifer, as well as it may promote other processes. In this study, we deal with hydrochemical and isotopic analysis of groundwater samples from four distinct zones in Catalonia (NE Spain), which include different lithological units, to investigate the influence of manure fertilization on the overall hydrochemical composition of groundwater. Results indicate that high nitrate concentrations, resulting from intense manure

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application, homogenize the contents of the major dissolved ions (i.e.;  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ ). Moreover, positive linear relationships between nitrate and some ions are found indicating the magnitude of the fertilization impact on groundwater hydrochemistry. Nevertheless, the increasing concentration of specific ions is not only attributed to the manure input, but to the enhancing effect of manure and slurry upon the biogeochemical processes that control water-rock interactions. Such results raise awareness that such processes should be evaluated in advance in order to assess adequate groundwater resources assessment.

### Highlights

- The effects of nitrate pollution have been evaluated in five different aquifer types
- Statistical and multivariate analyses are used to identify groundwater changes
- Agricultural pollution modifies groundwater conditions and geochemical processes

## INTRODUCTION

Nitrate occurrence and transport in aquifers have been widely studied since it is one of the major threats in groundwater, and most aquifers in agricultural areas are affected by this contaminant (Spalding and Exner, 1993; EEA, 2012). Most of the papers that focused on nitrate pollution study, by means of hydrochemical and isotopic data, nitrate trends in groundwater at different scales to identify potential sources of pollution and build-up hydrogeochemical models to understand the behavior of nitrate polluted aquifers (for instance, Burg and Heaton, 1998; Hudak, 2000; Katz et al., 2004; Masetti et al., 2008; Vitòria et al., 2008; Carbó et al., 2009; Kaown, et al., 2009; Menció et al., 2011; Boy-Roura et al., 2013). However, agricultural pollution due to a long and continued application of organic fertilizer (slurry and manure) may not only entail an increase on this ion in aquifers. On the one hand, other substances present in manure also enter into the groundwater system, such as

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ions, metals, emerging organic contaminants, or even microorganisms. On the other hand, these substances interact with the subsurface environment, modifying groundwater conditions, enhancing geochemical processes and even modifying groundwater communities (Cho et al., 2000; Böhlke, 2002; Murray et al., 2010; Stein et al., 2010; Korbel and Hose, 2011; Lapworth et al., 2012; Korbel et al., 2013; Choi et al., 2013).

In this study, we look for the evidence of the changes that manure application exerts on the major components concentrations by conducting an analysis of a large hydrochemical database, including isotopic data, of nitrate polluted aquifers representative of several geological environments. Our aim is to analyze whether manure and slurry application lead to a loss of the hydrogeological fingerprint of the geological background, and whether the resulting groundwater composition is only caused by mixing with manure lixiviates or by changes in biogeochemical processes.

Manure applied as fertilizer has a complex chemical composition. For instance, Vitòria (2004) analyzed its composition from several farms in Osona (Catalonia, NE Spain) and reported that the concentration of some major inorganic components in pig manure, the most used organic fertilizer in the studied areas in Catalonia (NE Spain), is notably larger than their natural values in groundwater. This is the reason why its impact on groundwater hydrochemistry must be evaluated to avoid misinterpretation of supposedly hydrochemical natural data.

Samples for this study belong to four distinct regions in Catalonia, all of them classified as Nitrate Vulnerable Zones (NVZs) as a result of the transposition of the Nitrate Directive (ND) 91/676/EC. In fact, NVZs in Catalonia cover up to 40% of the total area, and half of them show nitrate concentrations higher than 40 mg/L, affecting 17 out of the 53 groundwater bodies which are at risk of not meeting the European Water Framework Directive goals (ACA, 2007; Boy-Roura, 2013). In this study, we analyze datasets from the

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75 following NVZs, according to published results in the Selva basin (Folch et al., 2011; Menció  
76 et al., 2012; Puig et al., 2013), Empordà basin (Puig, 2014), Osona region (Vitòria et al.,  
77 2008; Otero et al., 2009; Menció et al., 2011; Boy-Roura et al., 2013), and Garrotxa area  
78 (based on still unpublished data). According to their lithologies, five groups of aquifers are  
79 distinguished (Figure 1 and Figure 2):

- 80 • Group 1: Aquifers in igneous rocks, especially granite and granodiorite and, in a  
81 lesser degree, in metamorphic rocks such as shale, schist, marble, and gneiss. These  
82 aquifers are mainly located in the ranges surrounding the Selva and Empordà basins.  
83 Hydrochemically, they present  $\text{Ca}^{2+}\text{-HCO}_3^-$  and  $\text{Ca}^{2+}\text{-HCO}_3^-\text{-Cl}^-$  facies, tending to  
84 evolve to  $\text{Na}^+\text{-HCO}_3^-$ .
- 85 • Group 2: Aquifers in sedimentary rocks, mainly Paleogene sedimentary rocks,  
86 including detritic, organic and chemical sedimentary rocks, such as conglomerates,  
87 sandstones, siltstones, limestones, marls, and gypsum deposits. Although these  
88 aquifers are present in all the study areas, they are mainly exploited in Osona and  
89 Garrotxa, and with a minor extent in Empordà. Main hydrochemical facies are  $\text{Ca}^{2+}\text{-}$   
90  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$  or  $\text{Ca}^{2+}\text{-SO}_4^{2-}$ .
- 91 • Group 3: Aquifers in sediments derived from igneous and metamorphic rocks. The  
92 arkosic sands, gravels and silt layers of the Neogene deposit that filled the Empordà  
93 and Selva areas, and the more recent Quaternary alluvial formations associated to the  
94 main rivers in these basins, are the weathering products of the main range areas,  
95 mainly located in the Pyrenees Montseny-Guilleries and Gavarres ranges. They show  
96 similar facies than Group 1.
- 97 • Group 4: Aquifers in sediments derived from sedimentary rocks. These aquifers are  
98 located in Osona and Garrotxa basins, and constitute the Quaternary alluvial aquifers  
99 and surface formations in these areas. Their facies are analogous to those of Group 2.



- 100 • Group 5: Aquifers in volcanic materials. In this group of aquifers there is a broad  
101 variety of materials, from phreatomagmatic and pyroclastic deposits to basaltic lava  
102 flow locally interleaved by sedimentary (alluvial) levels, which may locally be the  
103 most productive units. These materials are mainly located in the Garrotxa area, but  
104 volcanic lithologies also constitute aquifers in some parts of the Selva basin. This  
105 group shows the lowest EC values with  $\text{Ca}^{2+}\text{-HCO}_3^-$  or  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$  facies.

## 107 **METHODOLOGY**

108 Field surveys, in the studied datasets (Folch et al., 2011; Menció et al., 2012; Puig et al.,  
109 2013; Puig, 2014; Otero et al., 2009; Menció et al., 2011; Boy-Roura et al., 2013), were  
110 conducted from 2006 to 2013. A total number of 204 groundwater sampling locations  
111 constitute the whole dataset –distributed as Selva basin: 37 samples; Empordà basin: 45;  
112 Osona region: 57; Garrotxa area: 65– and they are classified according to the five described  
113 lithological groups (Table 1).

114 Similar analytical procedures for hydrochemical and isotopic analysis were followed at each  
115 studied region. Specific details are described in each of the given references. Concentration  
116 units are reported in mg/L. Most of the samples had an ionic mass balance error between  
117  $\pm 5\%$ . Isotope  $\delta$ -notation for water isotopes is expressed in terms of the ‰ deviation of the  
118 isotope ratio of the sample relative to that of the V-SMOW standard. Analytical errors are  
119  $\pm 0.06\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 0.7\text{‰}$  for  $\delta\text{D}$ . Nitrate isotope notation is also expressed in terms of  $\delta$   
120 ( $\text{‰}$ ) relative to that of the international standards AIR (atmospheric  $\text{N}_2$ ) for  $\delta^{15}\text{N}$ . Precision  
121 ( $\equiv 1\sigma$ ) of the samples are  $\pm 0.3\text{‰}$  and  $\pm 0.4\text{‰}$ , for  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ , respectively.

122 The SPSS program (version 19, 2010, SPSS Inc.) was used to conduct the different statistical  
123 analyses. Differences between aquifer hydrochemical parameters were analyzed considering  
124 the Kruskal-Wallis and Mann-Whitney U tests, for non-parametric data, since none of the

125 parameters were normally distributed. In addition, a Principal Component Analysis (PCA)  
126 was conducted in order to identify associations between variables and samples. The  
127 associations obtained through a PCA, based on similar magnitudes and variations in  
128 chemical, physical, and isotopic values in the groundwater samples composition, are adequate  
129 to indicate the influence of human factors, hydrochemical processes, or even, the origin of  
130 groundwater (for instance, Helena et al., 2000; Menció and Mas-Pla, 2008; Menció et al.,  
131 2013; Re et al., 2014).

## 133 **RESULTS AND DISCUSSION**

134 At a first glance, hydrochemical characteristics of groundwater samples with low  $\text{NO}_3^-$   
135 content (below the health standard limit of 50 mg  $\text{NO}_3^-/\text{L}$ ) reflect the dominant role of  
136 lithology in the composition, as observed in Figure 2. Mean and standard deviation values  
137 (Table 1) and boxplot shapes of selected parameters (EC,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ; Figure 2) for  
138 samples with low nitrate content, reflect the differences among aquifer types attributed to  
139 distinct lithology, showing the hydrochemical characteristics of groundwater samples under  
140 natural conditions. For instance, aquifers in groups 1 and 3, including igneous and  
141 metamorphic aquifers and sediments derived from these rocks, do not show significant  
142 differences between concentrations of the major hydrochemical components (with p-values  
143 between 0.089 and 0.881). These aquifers, for instance, present significant differences when  
144 compared with groups 2 and 4, representing aquifers in sedimentary rocks and in sediments  
145 derived from these rocks, for ions such as  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  (p-values ranging from values  
146  $<0.001$  to 0.038). Contrarily, hydrochemical characteristics of groundwater at high-nitrate  
147 concentrations ( $> 50$  mg  $\text{NO}_3^-/\text{L}$ ; Figure 2) seem to homogenize their concentrations despite  
148 lithological differences, presenting wider ranges for major ions distribution and erasing the

149 main differences in their hydrochemical composition of the distinct groups observed at low  
150  $\text{NO}_3^-$  samples.

151 In detail, when samples of low and high nitrate content for each lithological aquifer group are  
152 compared, significant higher EC values are observed in the most polluted wells (p-values  
153 ranging from 0.006 to values lower than 0.001). Higher EC values are related to significant  
154 higher concentrations of ions:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  (Table 1). An exception are samples  
155 of group 1, which do not show significant differences in any of these parameters between low  
156 and high nitrate groups (p-values ranging from 0.123 for  $\text{Ca}^{2+}$  to 0.877 for  $\text{Cl}^-$ ), since some of  
157 these samples belong to thermal and/or  $\text{CO}_2$ -rich systems. Geochemical evolution in such  
158 environments overlays the chemical contribution of manure inputs. In addition, it is worth  
159 mentioning that these  $\text{Cl}^-$  and  $\text{Na}^+$  higher concentrations are not detected in wells located in  
160 aquifer group 3 (in sediments derived from igneous and metamorphic rocks, and p-values of  
161 0.684 and 0.844, respectively), where natural processes can also favor high  $\text{Cl}^-$  and  $\text{Na}^+$   
162 concentrations.

163 It is also relevant that fewer hydrochemical differences are detected when high nitrate  
164 concentration sample populations for the different aquifers are compared (Figure 2 and Table  
165 1). As expected due to lithological similarity, no significant differences are detected between  
166 groups 1 and 3 (p-values ranging from 0.087 for  $\text{SO}_4^{2-}$  and 0.906 for  $\text{Cl}^-$ ), neither between  
167 groups 2 and 4 (p-values between 0.050 for  $\text{HCO}_3^-$  and 0.732 for  $\text{SO}_4^{2-}$ ). Nevertheless, when  
168 samples with high nitrate concentrations of group 1 and 2 are compared, only significant  
169 differences in  $\text{SO}_4^{2-}$  and  $\text{K}^+$  are detected (p-values of 0.024 and 0.023), while other  
170 components show similar concentration ranges. Furthermore, differences among high nitrate  
171 concentrations samples of groups 1 and 4 are only evident for  $\text{Ca}^{2+}$  and  $\text{K}^+$  (p-values of 0.018  
172 and 0.011); comparing samples of groups 2 and 3, significant differences are reduced to  $\text{Mg}^{2+}$   
173 and  $\text{K}^+$  (with p-values  $<0.001$ ); and, differences between samples of groups 1 and 5 with high

174 nitrate concentrations are significant for  $\text{Na}^+$  and  $\text{K}^+$  (p-values of 0.014 in both cases). Indeed,  
175 this group 5 shows the largest differences with the rest of the aquifer groups for high  $\text{NO}_3^-$   
176 samples. In volcanic materials, nitrate pollution is clearly lower than in the rest of the studied  
177 aquifers, with an overall mean value of  $30.90 \pm 3.81$  mg/L (Table 1). In this case, high nitrate  
178 concentration samples presented differences with respect to nitrate for samples of groups 2, 3  
179 and 4 (p-values of 0.026, 0.027 and 0.031, respectively). Between group 5 and these other  
180 groups, significant differences were also observed in EC,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  (p-values  
181 ranging from  $<0.001$  to 0.044); besides, significant differences were detected between group  
182 5 and groups 2 and 3 for  $\text{Ca}^{2+}$  (p-values  $<0.001$ ); and, with group 3 for  $\text{K}^+$  and  $\text{Mg}^{2+}$  (p-values  
183 of 0.008 and 0.004, respectively) .

184 Complementarily, two Principal Component Analyses were conducted to determine the  
185 different relationships among samples and variables. The first one considered all available  
186 samples, a total number of 204; and considered eleven variables, including: EC, pH, total  
187 aqueous concentration of  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ , and  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . In the  
188 second analysis, the dataset included only those samples that, in addition to the mentioned  
189 variables, also included nitrate isotopic data ( $\delta^{15}\text{N}_{\text{NO}_3}$ ). In this analysis the number of samples  
190 was reduced to 158, as in 32% of them (mainly from group 5) lacked the nitrate isotopic  
191 information. By conducting both statistical analyses we seek illustrating whether  
192 denitrification processes are relevant on the understanding of the hydrochemical changes in  
193 groundwater related to nitrate pollution. This is the reason why both analyses are shown  
194 herein, and compared.

195 In the first PCA, variables as pH,  $\text{HCO}_3^-$ ,  $\text{K}^+$  and  $\delta\text{D}$  were ruled out of in order to obtain  
196 better values of the goodness-of-fit statistics. Thus, a PCA conducted with the 7 remaining  
197 variables had a Barlett chi-square statistic of 1241.6 (for 28 degrees of freedom and a  
198 minimum significance level of  $<0.001$ ), and a value of sampling adequacy (MSA) obtained

199 by the Kaiser-Meyer-Olkin of 0.732. In the second analysis, the final solution considered 8  
200 variables, and had a better fit with a Barlett chi-square statistic of 1085.5 (for 36 degrees of  
201 freedom and a minimum significance lower than 0.001), and a MSA of 0.758.

202 Four varifactors (VF) were obtained in both analyses, explaining 91.59% and 88.19% of the  
203 total variance, respectively. In each PCA, these varifactors explained the same processes and  
204 associations of variables; excepting natural attenuation, which was only considered in the  
205 second one as  $\delta^{15}\text{N}_{\text{NO}_3}$ . For this reason, only the scores and samples distribution obtained in  
206 the second PCA are shown in Table 2 and Figure 3. Thus, after a Varimax rotation, the final  
207 VFs were interpreted as follows:

- 208 • VF1 includes  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and EC, explaining a 32.53% of the total variance.  
209 This VF1 stands for water-rock interaction processes, specifically in sedimentary  
210 formations where gypsum dissolution occurs, since VF1 highest values are obtained  
211 in samples located in aquifers belonging to groups 2 and 4, where these processes  
212 have been described to govern groundwater hydrochemistry (Figure 3a; Menció et al.,  
213 2011; Soler et al., 2014).
- 214 • VF2 represents the 20.41% of variability of the data. It mainly includes  $\text{NO}_3^-$ , with a  
215 lower participation of  $\text{Ca}^{2+}$ , EC and  $\text{Cl}^-$ . VF2 has been interpreted as nitrate pollution,  
216 showing the direct relationship between  $\text{NO}_3^-$  and EC,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  variables.
- 217 • With a 20.23% of the total variance, VF3 is participated by  $\delta^{18}\text{O}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$ . This  
218 VF3 is linked to the recharge altitude of groundwater samples, with high scores in  
219 samples recharged at low altitude, and low scores in samples recharged at high  
220 altitude. In addition, it is worth recalling that recharge areas of most of the wells  
221 drilled in igneous and metamorphic rocks and in the sediments derived from them  
222 (groups 1 and 3) are located at low altitude. Because of their lithology, water samples

223 present high concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$ , explaining the association of both ions  
224 with  $\delta^{18}\text{O}$  (Table 1, Figure 2 and Figure 3).

- 225 • VF4 is mainly associated to  $\delta^{15}\text{N}_{\text{NO}_3}$ , with a lower participation of  $\text{Na}^+$  and  $\text{Cl}^-$ . With a  
226 15.03% of the total variance explained, this last VF represents natural attenuation  
227 processes (i.e., denitrification). The association of  $\text{Na}^+$  and  $\text{Cl}^-$  with high  $\delta^{15}\text{N}_{\text{NO}_3}$   
228 values ( $\delta^{15}\text{N} > 15\text{‰}$ , according to Kendall et al., 2007) may be attributed to the  
229 attenuation processes described in the Selva basin, group 3, where regional flow  
230 systems with  $\text{Na}^+\text{-HCO}_3^-$  facies and reducing conditions, enhanced natural  
231 heterotrophic attenuation processes (Puig et al., 2013).

232 Two sample tendencies with positive scores for  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (that is, VF1) are  
233 distinguished in a plot VF1 vs. VF2. The first tendency presents high scores for VF2 as well,  
234 which links samples with high  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  content to high nitrate concentrations  
235 (quadrant I in Figure 3a), including samples from aquifer groups 2, 3 and 4 with nitrate  
236 concentrations between 280 to 590 mg  $\text{NO}_3^-/\text{L}$ . The second one is associated to negative  
237 values in VF2, and it is composed of samples from aquifer groups 2 and 4, those related to  
238 sedimentary rocks and the sediments derived from these materials. In this case, nitrate  
239 concentrations are notably lower, between 2.5 to 119 mg/L, and the sample with the highest  
240 VF1 score is the one with the lowest nitrate concentration. Thus, two clear sets of samples  
241 with distinct origins for  $\text{SO}_4^{2-}$  are distinguished in these study areas: one with  $\text{SO}_4^{2-}$  related to  
242 nitrate pollution, and the other with  $\text{SO}_4^{2-}$  related to natural sources.

243 In Figure 3b, high and low scores for nitrate pollution (VF2) are distributed in both high and  
244 low altitude recharge areas (as defined by  $\delta^{18}\text{O}$  isotopic compositions, VF3). This indicates a  
245 widespread nitrate distribution all over the study areas, being consistent with an intense  
246 agricultural activity. However, most of samples in aquifer group 5, which wells are located in

247 volcanic rocks, present low VF2 values, consistent with the comparatively low pollution  
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2 248 levels in this aquifer type (Table 1).  
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4 249 Finally, when nitrate content (VF2) and nitrate attenuation (VF4) are plotted (Figure 3c),  
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7 250 samples with the highest nitrate concentration (with values exceeding 150 mg NO<sub>3</sub><sup>-</sup>/L at VF2  
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9 251 scores > 1) are located in quadrants I and II; while quadrants I and IV include those samples  
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11 252 affected by natural attenuation (with δ<sup>15</sup>N>15‰). Samples of quadrant I and IV indicate that  
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13 253 attenuation processes are active independently of the nitrate concentration. Besides, in some  
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15 254 cases, nitrate content has been reduced to values lower than the health standard limits of 50  
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17 255 mg/L, as represented by the sample with negative scores of VF2. These nitrate attenuation  
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19 256 processes have been detected in all aquifers types.  
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24 257 Bivariate plots of selected ions against nitrate concentrations point out their linear increase  
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26 258 proportional to manure application. SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> (both included in VF1) and Cl<sup>-</sup>  
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28 259 (participating in VF2 and VF3) as major components illustrate this fact (Figure 4). Linear  
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30 260 regression equations are estimated for each aquifer lithology using all the available data,  
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32 261 despite their δ<sup>15</sup>N<sub>NO<sub>3</sub></sub> value. Such regression equations prevail over two facts: 1) the inherent  
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34 262 variability of the manure chemical composition depending on its origin and storage before  
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36 263 application; and 2) the heterogeneity of soil processes, which are different, in type and  
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38 264 magnitude, depending on the soil nature and the crop type. Therefore, equations indicate the  
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40 265 rate of ion concentration changes with increasing nitrate content (slope); that is, the amount  
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42 266 of each ion that any unit of nitrate adds to groundwater whether as a direct input or as a result  
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44 267 of enhancing geochemical processes; and the expected value of the major component where  
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46 268 no fertilization occurs (y-intercept). Such linear increase is quite evident for these three ions,  
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48 269 and similar relationships occur for other major components.  
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51 270 Nevertheless, each geological environment show distinct responses to nitrate inputs. Water-  
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53 271 rock interaction in igneous and metamorphic rocks (group 1) will depend on the low  
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272 solubility of silicate minerals, and of other processes as cation exchange, which may  
273 significantly alter the  $\text{Ca}^{2+}:\text{Na}^+$  ratio and it may be responsible for a wide dispersion of data  
274 values with and without the occurrence of nitrate pollution. The large heterogeneity of  
275 volcanic deposits (group 5), which may include sedimentary layers among volcanic episodes,  
276 also originates a wide range of geochemical values as regards of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . However,  
277  $\text{Cl}^-$  concentration in the studied aquifers appears to be well related to manure fertilization.  
278 Moreover, the occurrence of thermal and/or  $\text{CO}_2$ -rich waters in group 1 aquifers may enhance  
279 specific weathering processes resulting, for instance, in large chloride concentrations that  
280 infiltrating water may dilute.

281 As already suggested by the PCA results,  $\text{SO}_4^{2-}$  content may originate from evaporitic rocks  
282 (gypsum) dissolution or from manure contribution. These two geochemical paths are also  
283 recognized in groups 2 and 4, where sedimentary rocks or their denudation deposits constitute  
284 the aquifers: significantly large values of  $\text{SO}_4^{2-}$  are found at low nitrate concentration ( $<75$   
285  $\text{mg NO}_3^-/\text{L}$ ), whereas a clear linear relationship between them appears as nitrate content  
286 increases. Correlation factors, as they appear in Figure 4, are misleading since they represent  
287 the whole dataset; exclusion of those points largely affected by gypsum dissolution will turn  
288 to larger  $R^2$  values proving the influence of manure fertilization on the final groundwater  
289 composition.

290 Denitrification processes also affect such bivariate relationships. In those places where  
291 autotrophic nitrate reduction has been proved (group 2 samples, Osona region; Otero et al.,  
292 2009), an increase of  $\text{SO}_4^{2-}$  due to pyrite oxidation will occur coupled to nitrate decrease;  
293 whereas heterotrophic attenuation processes will increase alkalinity. Both processes will also  
294 have consequences on the gypsum and calcite equilibriums modifying the  $\text{Ca}^{2+}$  concentration,  
295 yet the neat linear increase of  $\text{Ca}^{2+}$  with nitrate in most of the aquifer types might suggest that  
296 it directly originates in the manure itself. However, a geochemical insight to calcium



297 equilibrium indicates that nitrification of reduced N from manure generates acidity along with  
298  $\text{NO}_3^-$  and it enhances carbonate dissolution. This process can even be accentuated where lime  
299 or dolomite are applied as soil neutralizers in agricultural lands (Böhlke, 2002; Choi et al.,  
300 2013), increasing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. Complementarily, the analysis of  
301 hydrochemical evolution of pig manure stored in experimental pits showed a decrease of  $\text{Ca}^{2+}$   
302 and  $\text{Mg}^{2+}$  through time (Vitòria, 2004). Since manure is usually stored for several months  
303 before its application,  $\text{Ca}^{2+}$  increase shown in Figure 4 may be better attributed to  
304 geochemical reactions occurring in the soil and in the subsurface following fertilization than  
305 to direct manure contribution. Hence, the observed hydrochemical composition is not just a  
306 simple conservative mixture of groundwater with infiltrating slurry and manure lixiviation.  
307 Contrarily,  $\text{Na}^+$  and  $\text{K}^+$  showed a conservative behavior in the liquid manure, being their  
308 concentrations increased by evaporation (Vitòria, 2004). However, groundwater samples are  
309 not specifically rich in both cations (Figure 2), suggesting that other processes as plant  
310 uptake, sorption and cation exchange may control their final content in groundwater (Böhlke,  
311 2002).

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## 313 CONCLUSIONS

314 Data from aquifers with distinct lithological environments prove that manure application as  
315 fertilizer modifies groundwater hydrochemical composition, turning it notably distinct than  
316 the expected natural background given by water-rock interaction and other natural processes.  
317 Manure and slurry fertilization homogenize the overall hydrochemistry despite lithological  
318 differences, hindering the geochemical interpretation inherent to any regional groundwater  
319 resources evaluation study.  
320 Nevertheless, such compositional modifications which, in general, tend to adopt a linear  
321 increase (Figure 4, all data) cannot be solely attributed to the effect of direct manure inputs,

322 as fertilization may enhance or reduce geochemical processes that control groundwater  
323 composition at equilibrium. Therefore accepting that nitrate pollution influences,  
324 groundwater regional reports should look for the relationships shown in these aquifers;  
325 checking potential influences upon the expected (natural) hydrochemical composition, so a  
326 better understanding of the hydrogeological system is attained.

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443 **FIGURE CAPTIONS**

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2 444 **Figure 1:** Geographical and geological setting of the distinct study areas.

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4 445 **Figure 2.** Box plots of the main hydrochemical parameters according to the aquifer groups  
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7 446 and nitrate concentrations ranges: Low nitrate concentrations refer to values below 50 mg/L,  
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9 447 and high nitrate concentrations refer to values above 50 mg/L (see SI2 for details). Legend:  
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11 448 Boxes represent the 25 and 75 percentiles and the median; while a white line represents the  
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13 449 mean value. Bars define the 10 and 90% percentile, and dots refer to extreme values.

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16 450 **Figure 3.** PCA scores distribution of the different samples, considering denitrification,  
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19 451 plotted according the lithological group and the  $\delta^{15}\text{N}_{\text{NO}_3}$ , content: a) VF1 vs VF2, b) VF3 vs  
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21 VF2, and c) VF4 vs VF2.

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24 453 **Figure 4.** Bivariate relationships of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  vs.  $\text{NO}_3^-$ . Linear regression equations  
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26 454 are calculated for all the samples of the group, disregarding their  $\delta^{15}\text{N}$  value. *Legend:* red  
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28 455 circles, samples with  $\delta^{15}\text{N} > 15\text{‰}$ ; black circles, samples with  $\delta^{15}\text{N} < 15\text{‰}$ ; white circles,  
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30 456 samples with  $\delta^{15}\text{N}$  data not available.

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## 459 TABLES

460 **Table 1:** Mean values and standard errors of the main physicochemical characteristics of the  
 461 different aquifer groups, differentiating samples of low and high nitrate content.

	G1- Igneous and metamorphic rocks		G2- Sedimentary rocks		G3- Aquifers derived from igneous and metamorphic rocks		G4- Aquifers derived from sedimentary rocks		G5- Volcanic materials	
	<50 mg/L	>50 mg/L	<50 mg/L	>50 mg/L	<50 mg/L	>50 mg/L	<50 mg/L	>50 mg/L	<50 mg/L	>50 mg/L
Number of wells	9	4	28	36	15	27	22	29	29	5
EC ( $\mu\text{S}/\text{cm}$ )	819 $\pm$ 110	915 $\pm$ 135	819 $\pm$ 70	1124 $\pm$ 65	841 $\pm$ 72	1073 $\pm$ 78	770 $\pm$ 27	1070 $\pm$ 64	623 $\pm$ 21	779 $\pm$ 31
pH	7.18 $\pm$ 0.14	6.99 $\pm$ 0.04	7.35 $\pm$ 0.09	7.43 $\pm$ 0.06	7.47 $\pm$ 0.12	7.28 $\pm$ 0.08	7.18 $\pm$ 0.04	7.08 $\pm$ 0.04	7.47 $\pm$ 0.06	7.25 $\pm$ 0.21
Eh (mV)	236.7 $\pm$ 62.1	386.5 $\pm$ 39.3	190.1 $\pm$ 20.1	247.4 $\pm$ 27.4	354.9 $\pm$ 38.7	379.8 $\pm$ 8.3	161.0 $\pm$ 13.5	164.3 $\pm$ 17.3	274.6 $\pm$ 21.0	240.0 $\pm$ 10.0
T ( $^{\circ}\text{C}$ )	17.4 $\pm$ 0.5	16.9 $\pm$ 0.3	15.4 $\pm$ 0.6	15.9 $\pm$ 0.4	16.3 $\pm$ 0.4	16.4 $\pm$ 0.2	15.1 $\pm$ 0.4	13.2 $\pm$ 0.2	14.5 $\pm$ 0.6	14.5 $\pm$ 0.4
O <sub>2</sub> (mg/L)	1.5 $\pm$ 0.6	3.9 $\pm$ 1.4	4.0 $\pm$ 0.6	4.0 $\pm$ 0.5	3.7 $\pm$ 1.1	5.2 $\pm$ 0.5	4.6 $\pm$ 0.6	4.4 $\pm$ 0.4	8.0 $\pm$ 0.6	7.6 $\pm$ 1.3
HCO <sub>3</sub> <sup>-</sup> (mg/L)	368.1 $\pm$ 59.6	346.9 $\pm$ 40.0	418.3 $\pm$ 15.4	388.0 $\pm$ 13.0	355.1 $\pm$ 34.4	360.7 $\pm$ 13.5	411.9 $\pm$ 18.6	407.4 $\pm$ 13.1	284.8 $\pm$ 13.0	341.7 $\pm$ 39.0
Cl <sup>-</sup> (mg/L)	101.0 $\pm$ 24.7	99.2 $\pm$ 42.8	42.4 $\pm$ 6.7	94.9 $\pm$ 10.4	86.1 $\pm$ 15.1	91.8 $\pm$ 11.9	16.0 $\pm$ 1.6	73.3 $\pm$ 12.4	16.1 $\pm$ 2.2	30.7 $\pm$ 10.4
SO <sub>4</sub> <sup>2-</sup> (mg/L)	35.9 $\pm$ 5.7	57.2 $\pm$ 8.6	132.4 $\pm$ 46.4	164.3 $\pm$ 32.1	68.4 $\pm$ 16.8	98.1 $\pm$ 12.4	43.5 $\pm$ 5.4	184.6 $\pm$ 34.6	48.0 $\pm$ 6.5	41.4 $\pm$ 8.2
NO <sub>3</sub> <sup>-</sup> (mg/L)	13.7 $\pm$ 4.2	105.3 $\pm$ 20.3	17.0 $\pm$ 2.5	166.3 $\pm$ 19.4	18.6 $\pm$ 4.4	137.5 $\pm$ 16.6	25.4 $\pm$ 2.7	172.2 $\pm$ 25.2	23.9 $\pm$ 2.4	71.4 $\pm$ 10.0
Na <sup>+</sup> (mg/L)	104.2 $\pm$ 38.0	79.7 $\pm$ 18.6	34.8 $\pm$ 4.2	54.3 $\pm$ 7.5	63.5 $\pm$ 12.0	56.4 $\pm$ 5.1	12.5 $\pm$ 1.4	42.0 $\pm$ 5.6	16.5 $\pm$ 1.5	21.5 $\pm$ .9
K <sup>+</sup> (mg/L)	2.2 $\pm$ 0.4	1.0 $\pm$ 0.3	4.4 $\pm$ 1.7	8.5 $\pm$ 2.4	2.4 $\pm$ 0.4	5.8 $\pm$ 3.0	2.8 $\pm$ 0.6	8.8 $\pm$ 2.1	7.6 $\pm$ 0.7	6.9 $\pm$ 1.7
Ca <sup>2+</sup> (mg/L)	82.6 $\pm$ 14.0	127.5 $\pm$ 21.5	132.6 $\pm$ 16.2	185.7 $\pm$ 10.1	110.7 $\pm$ 12.7	166.3 $\pm$ 9.7	135.8 $\pm$ 7.1	196.0 $\pm$ 10.8	87.2 $\pm$ 4.5	89.5 $\pm$ 8.4
Mg <sup>2+</sup> (mg/L)	14.6 $\pm$ 3.6	22.0 $\pm$ 3.5	37.4 $\pm$ 5.4	38.2 $\pm$ 3.8	19.3 $\pm$ 2.0	22.7 $\pm$ 2.4	21.0 $\pm$ 1.1	44.1 $\pm$ 5.6	19.5 $\pm$ 1.2	34.1 $\pm$ 3.5

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465 **Table 2.** Loadings obtained in the second PCA, including  $\delta^{15}\text{N}_{\text{NO}_3}$ , among the different  
 466 parameters.

	VF1	VF2	VF3	VF4
$\text{SO}_4^{2-}$ (mg/L)	<u>0.965</u>	0.008	-0.005	0.039
$\text{Mg}^{2+}$ (mg/L)	<u>0.885</u>	0.181	0.007	0.249
$\text{Ca}^{2+}$ (mg/L)	<u>0.740</u>	<u>0.562</u>	0.004	0.035
EC ( $\mu\text{S}/\text{cm}$ )	<u>0.641</u>	<u>0.546</u>	<u>0.425</u>	0.184
$\text{NO}_3^-$ (mg/L)	0.121	<u>0.949</u>	0.112	0.057
$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	-0.238	0.097	<u>0.848</u>	-0.178
$\text{Na}^+$ (mg/L)	0.295	0.054	<u>0.738</u>	<u>0.426</u>
$\text{Cl}^-$ (mg/L)	0.289	<u>0.520</u>	<u>0.601</u>	<u>0.405</u>
$\delta^{15}\text{N}_{\text{NO}_3}$ (‰)	0.113	0.085	0.047	<u>0.935</u>
Eigenvalue	2.928	1.837	1.821	1.352
% Variance	32.53	20.41	20.23	15.03

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Figure 1

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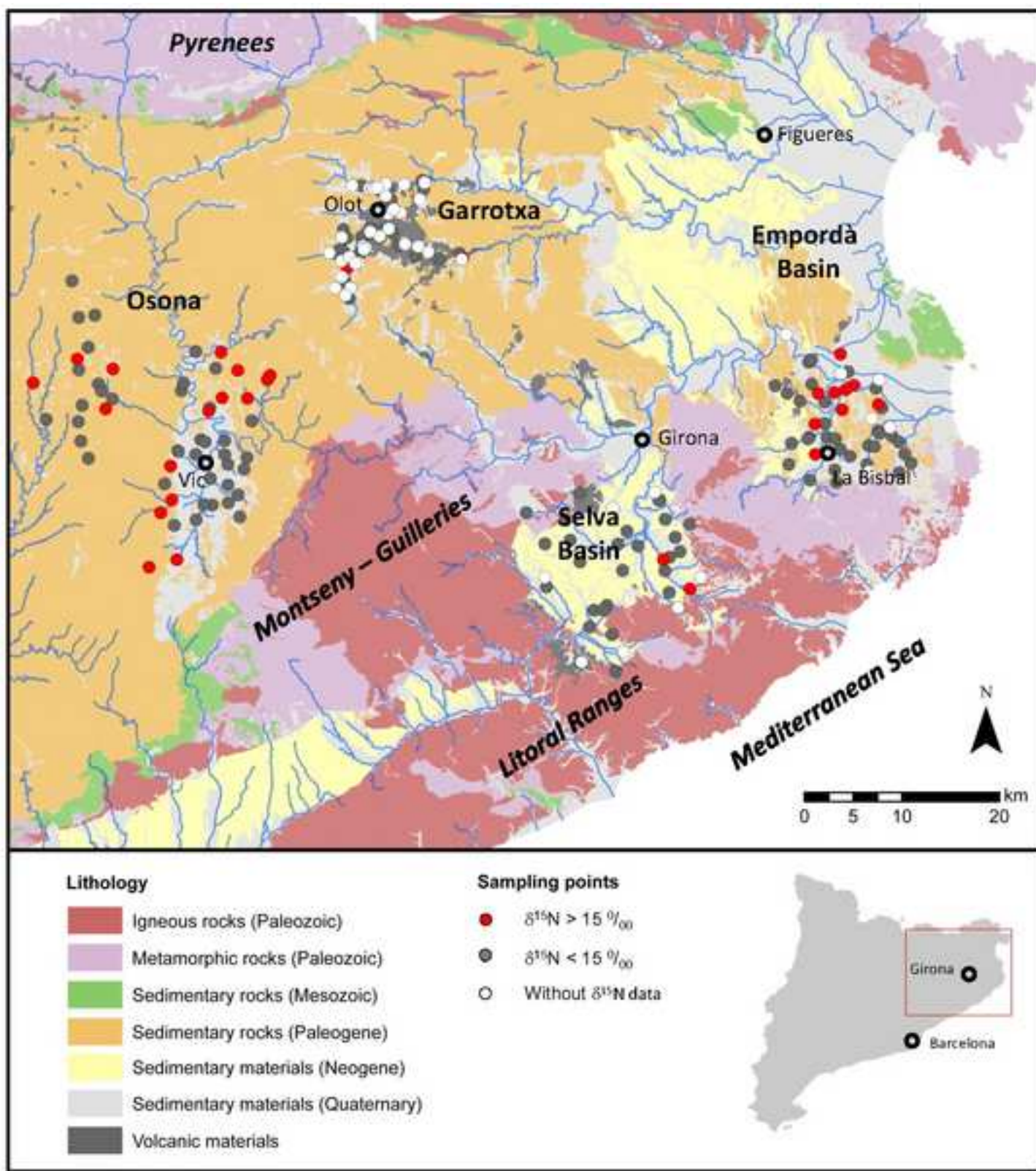


Figure 2  
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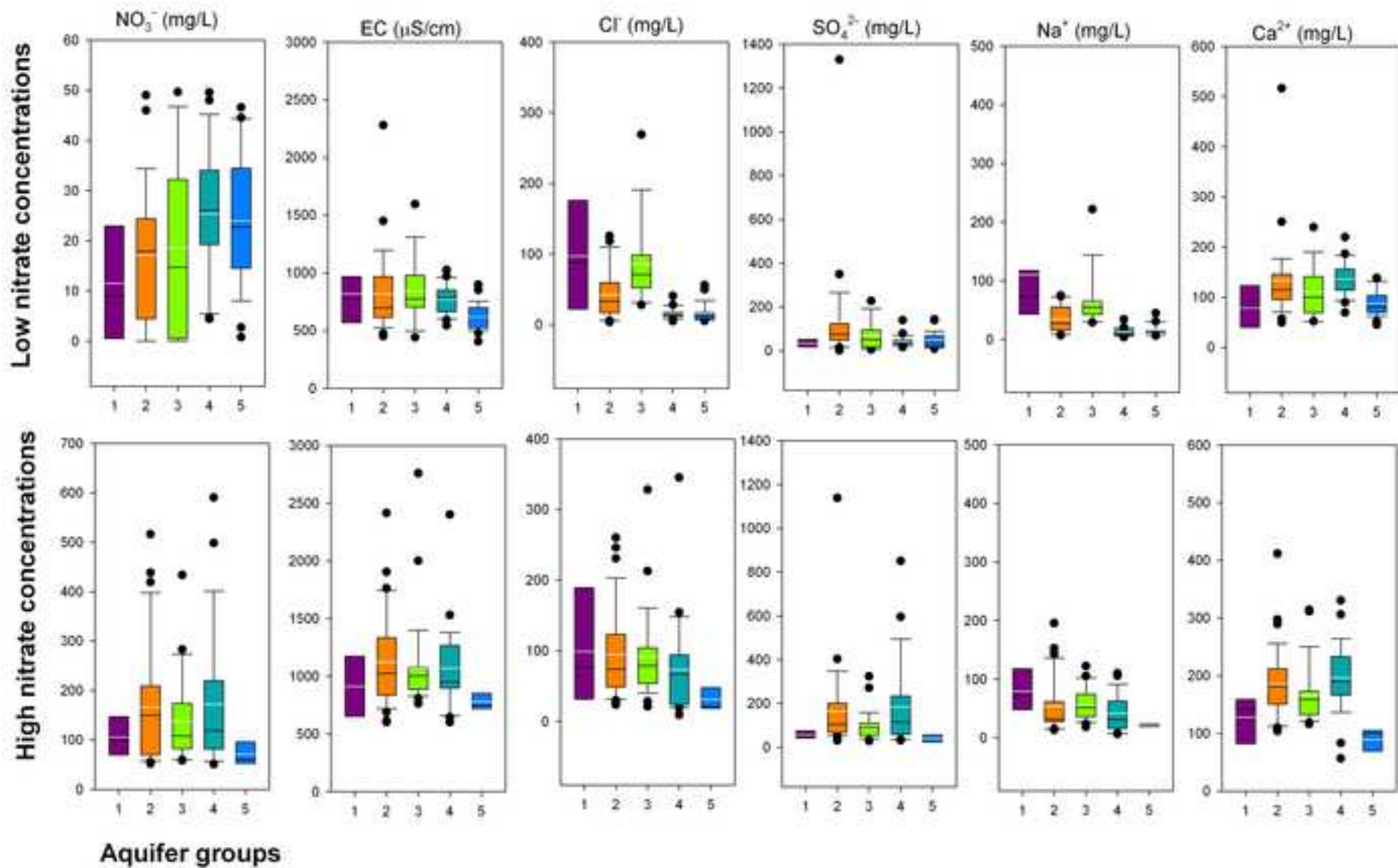


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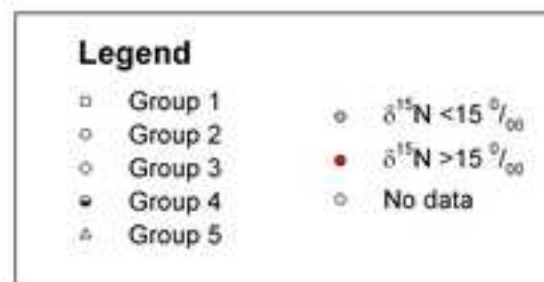
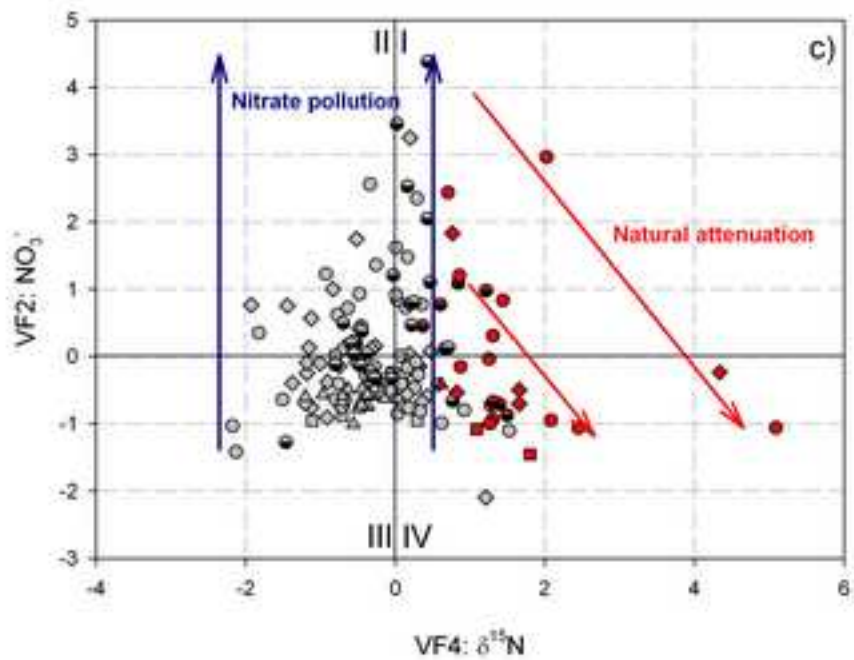
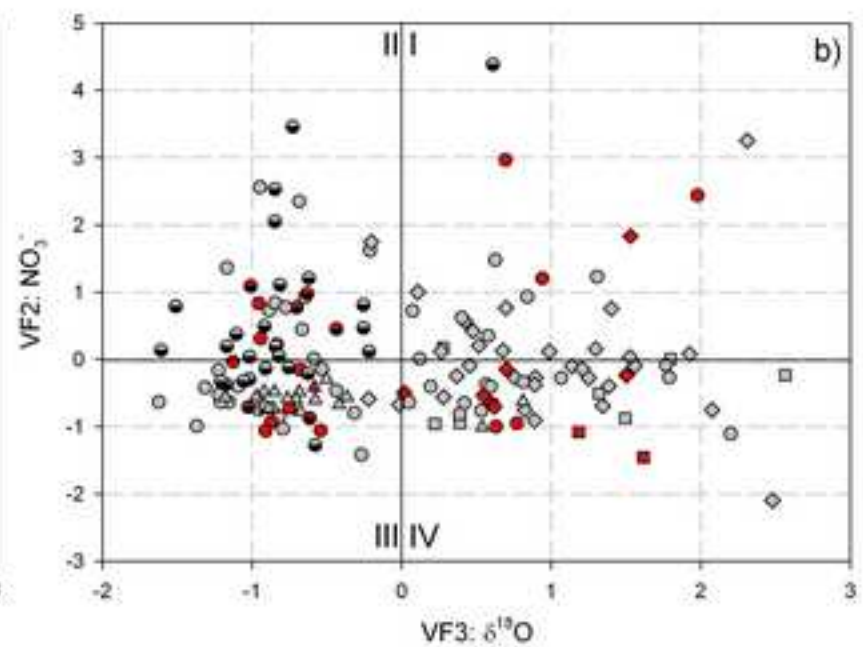
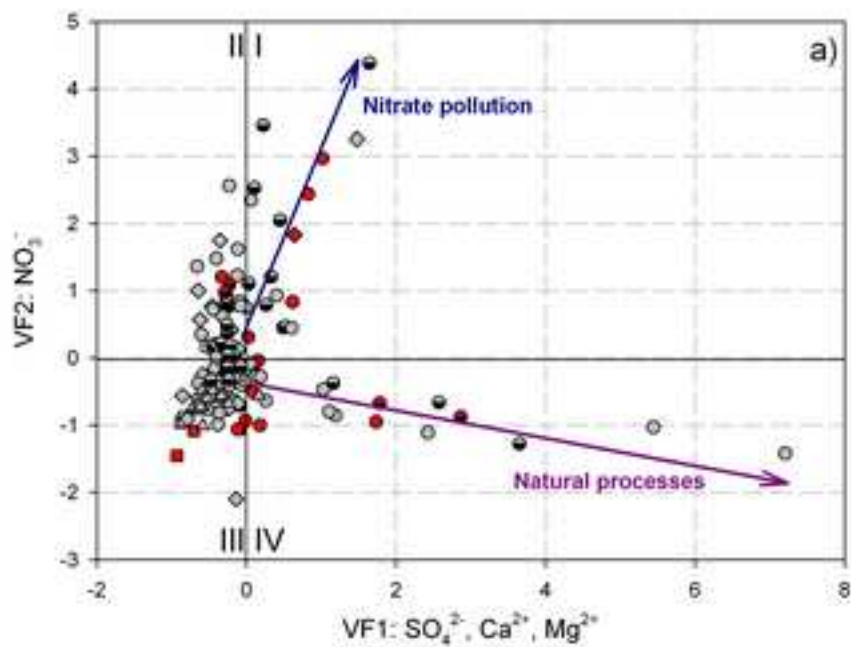


Figure 4  
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