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

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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⁻, SO₄²⁻, Ca²⁺, Na⁺, K⁺, and Mg²⁺). 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.

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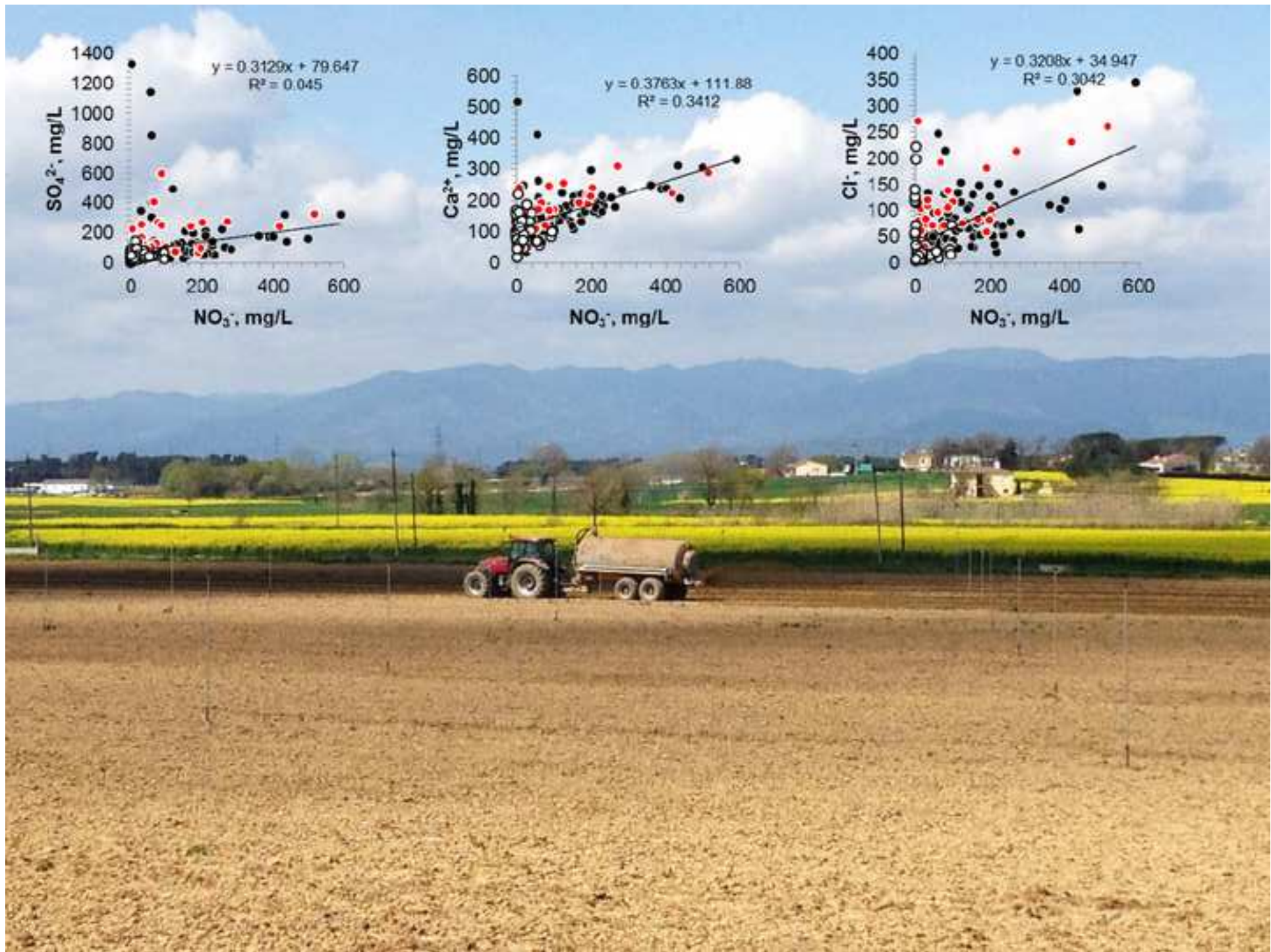
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Highlights

- 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

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

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34 16 **KEY WORDS:** nitrate pollution, hydrochemistry, water-rock interaction, multivariate
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37 18 **ABSTRACT**

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application, homogenize the contents of the major dissolved ions (i.e.; Cl^- , SO_4^{2-} , Ca^{2+} , Na^+ , K^+ , and 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 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.

- Group 5: Aquifers in volcanic materials. In this group of aquifers there is a broad variety of materials, from phreatomagmatic and pyroclastic deposits to basaltic lava flow locally interleaved by sedimentary (alluvial) levels, which may locally be the most productive units. These materials are mainly located in the Garrotxa area, but volcanic lithologies also constitute aquifers in some parts of the Selva basin. This group shows the lowest EC values with Ca^{2+} - HCO_3^- or Ca^{2+} - Mg^{2+} - HCO_3^- facies.

METHODOLOGY

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

Similar analytical procedures for hydrochemical and isotopic analysis were followed at each studied region. Specific details are described in each of the given references. Concentration units are reported in mg/L. Most of the samples had an ionic mass balance error between $\pm 5\%$. Isotope δ -notation for water isotopes is expressed in terms of the ‰ deviation of the isotope ratio of the sample relative to that of the V-SMOW standard. Analytical errors are $\pm 0.06\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.7\text{‰}$ for δD . Nitrate isotope notation is also expressed in terms of δ (‰) relative to that of the international standards AIR (atmospheric N_2) for $\delta^{15}\text{N}$. Precision ($\equiv 1\sigma$) 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.

The SPSS program (version 19, 2010, SPSS Inc.) was used to conduct the different statistical analyses. Differences between aquifer hydrochemical parameters were analyzed considering 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 NO_3^-
135 content (below the health standard limit of 50 mg NO_3^-/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, Cl^- , SO_4^{2-} , Na^+ , 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 Cl^- , Na^+ , and 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 NO_3^-/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 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: Cl^- , SO_4^{2-} , Na^+ and 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 Ca^{2+} to 0.877 for Cl^-), since some of
157 these samples belong to thermal and/or 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 Cl^- and 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 Cl^- and 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 SO_4^{2-} and 0.906 for Cl^-), neither between
167 groups 2 and 4 (p-values between 0.050 for HCO_3^- and 0.732 for SO_4^{2-}). Nevertheless, when
168 samples with high nitrate concentrations of group 1 and 2 are compared, only significant
169 differences in SO_4^{2-} and 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 Ca^{2+} and K^+ (p-values of 0.018
172 and 0.011); comparing samples of groups 2 and 3, significant differences are reduced to Mg^{2+}
173 and K^+ (with p-values <0.001); and, differences between samples of groups 1 and 5 with high

174 nitrate concentrations are significant for Na^+ and 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 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 ± 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, Cl^- , Ca^{2+} and 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 Ca^{2+} (p-values <0.001); and, with group 3 for K^+ and 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 HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ and K^+ , and $\delta^{18}\text{O}$ and δD . 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, HCO_3^- , K^+ and δD 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 SO_4^{2-} , Mg^{2+} , 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 NO_3^- , with a
215 lower participation of Ca^{2+} , EC and Cl^- . VF2 has been interpreted as nitrate pollution,
216 showing the direct relationship between NO_3^- and EC, Ca^{2+} and Cl^- variables.
- 217 • With a 20.23% of the total variance, VF3 is participated by $\delta^{18}\text{O}$, Na^+ and 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 Na^+ and 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 Na^+ and 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 Na^+ and 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 SO_4^{2-} , Ca^{2+} and 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 SO_4^{2-} , Ca^{2+} and 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 NO_3^-/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 SO_4^{2-} are distinguished in these study areas: one with SO_4^{2-} related to
242 nitrate pollution, and the other with 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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5 249 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 NO₃⁻/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 δ¹⁵N>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. SO₄²⁻ and Ca²⁺ (both included in VF1) and Cl⁻
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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 δ¹⁵N_{NO₃} 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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56 270 Nevertheless, each geological environment show distinct responses to nitrate inputs. Water-
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58 271 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 SO_4^{2-} and Ca^{2+} . However,
277 Cl^- concentration in the studied aquifers appears to be well related to manure fertilization.
278 Moreover, the occurrence of thermal and/or 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, 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 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 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 Ca^{2+} concentration,
295 yet the neat linear increase of 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 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 Ca^{2+} and Mg^{2+} concentrations. Complementarily, the analysis of
301 hydrochemical evolution of pig manure stored in experimental pits showed a decrease of Ca^{2+}
302 and Mg^{2+} through time (Vitòria, 2004). Since manure is usually stored for several months
303 before its application, 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, Na^+ and 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**

1
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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18 451 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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22 452 VF2, and c) VF4 vs VF2.

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24 453 **Figure 4.** Bivariate relationships of SO_4^{2-} , Ca^{2+} and Cl^- vs. 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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29 455 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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31 456 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 ₂ (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 ₃ ⁻ (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 ⁻ (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 ₄ ²⁻ (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 ₃ ⁻ (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 ⁺ (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 ⁺ (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 ²⁺ (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 ²⁺ (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
SO_4^{2-} (mg/L)	<u>0.965</u>	0.008	-0.005	0.039
Mg^{2+} (mg/L)	<u>0.885</u>	0.181	0.007	0.249
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
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
Na^+ (mg/L)	0.295	0.054	<u>0.738</u>	<u>0.426</u>
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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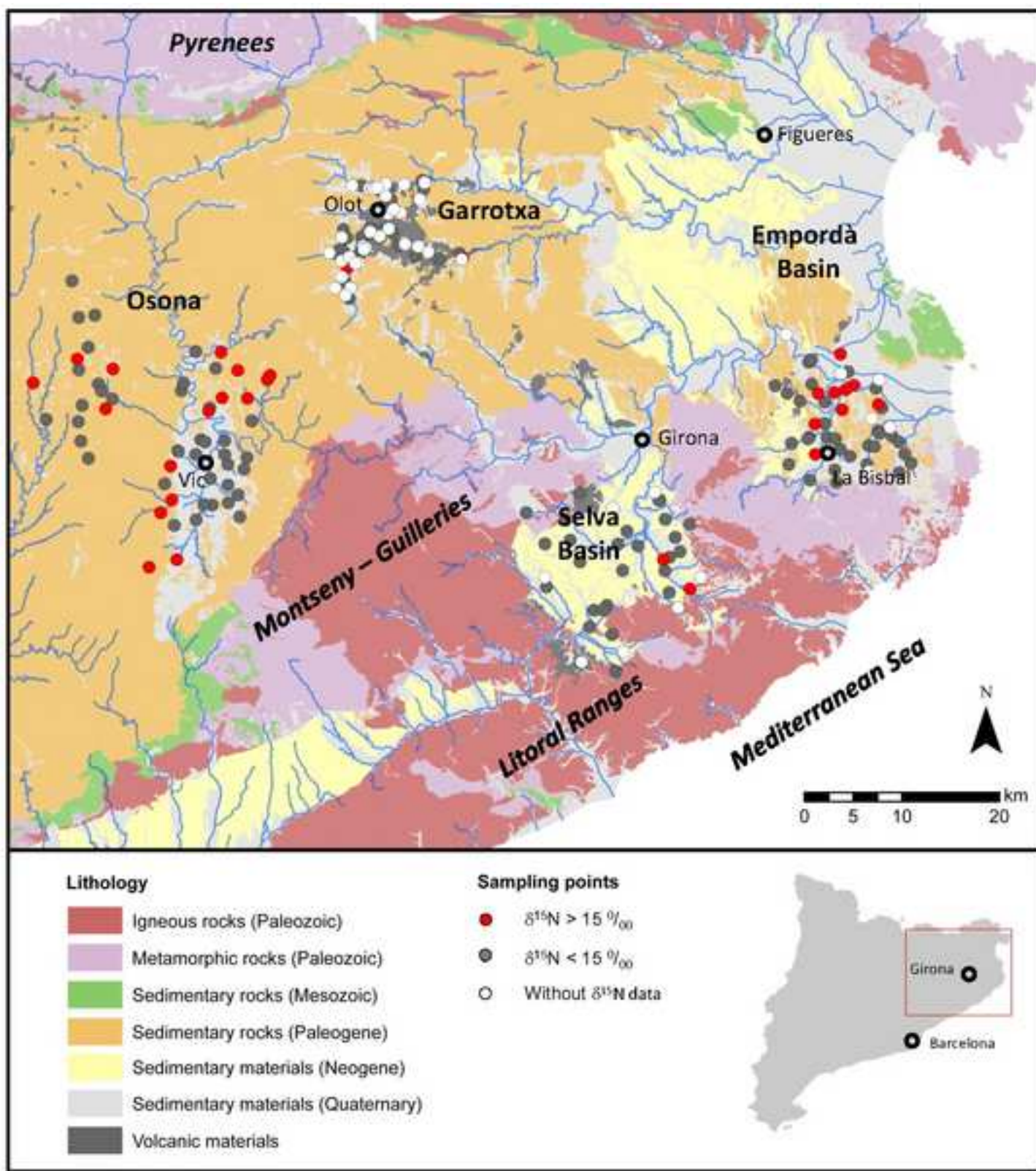


Figure 2
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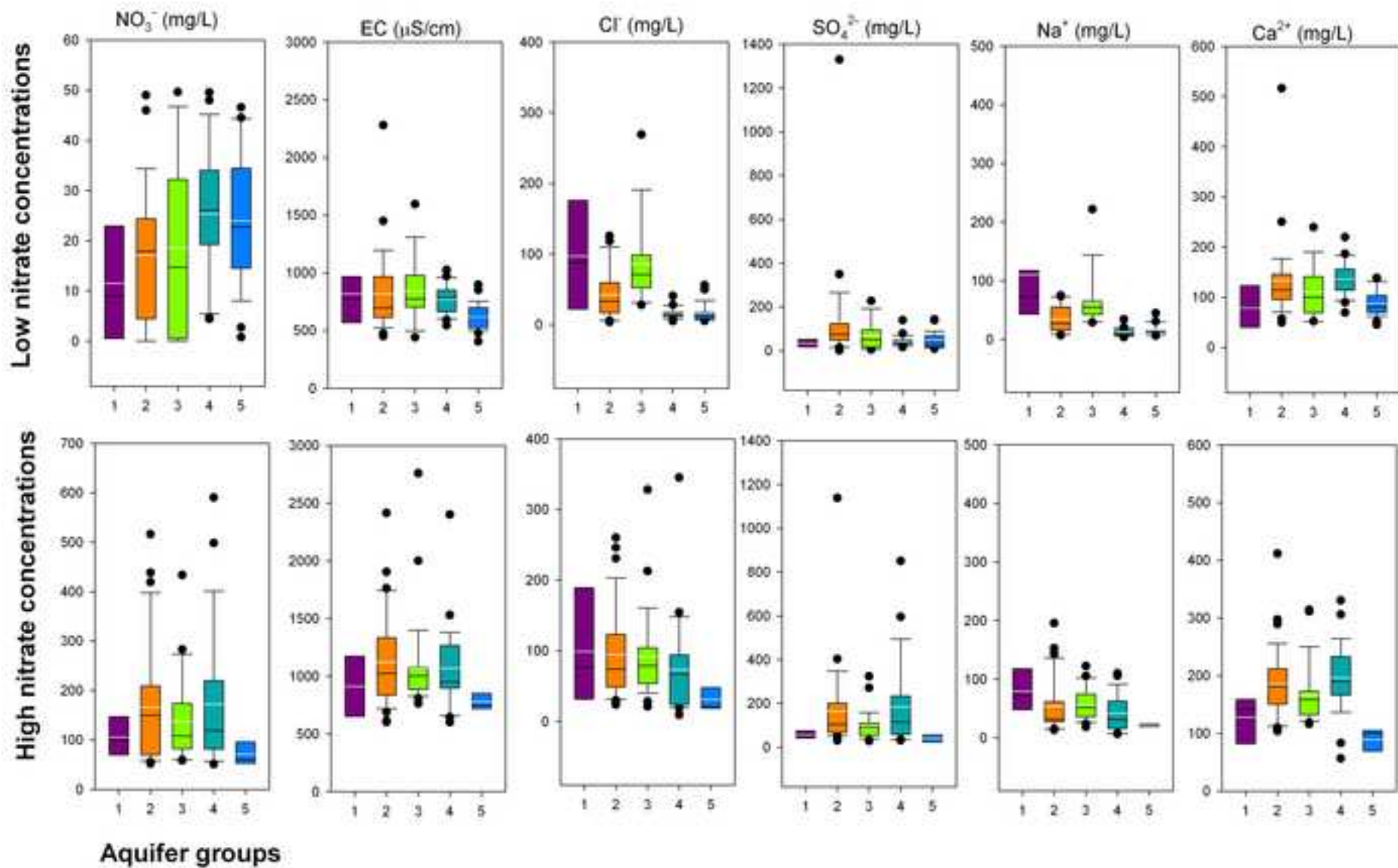


Figure 3
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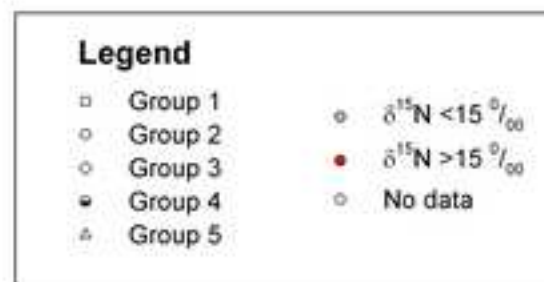
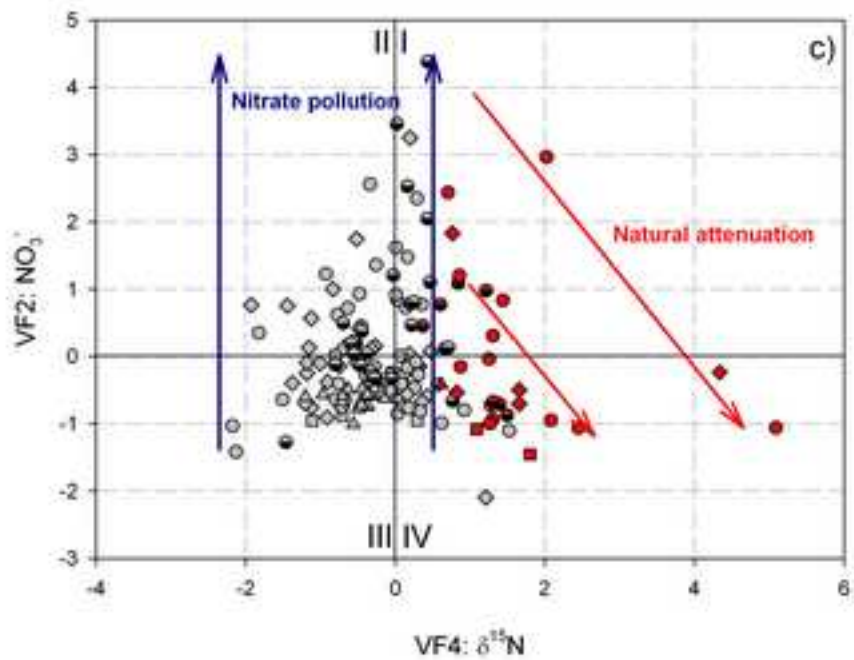
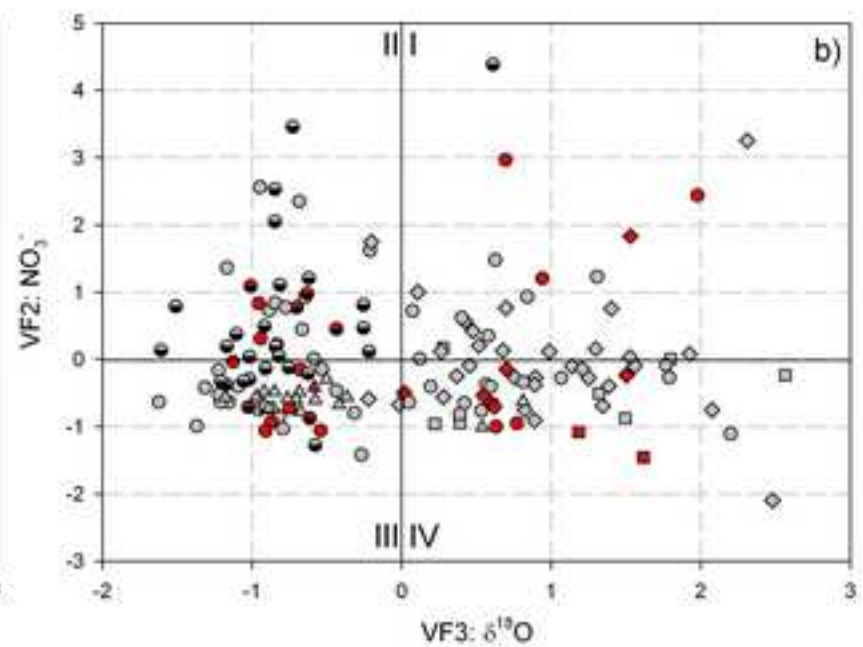
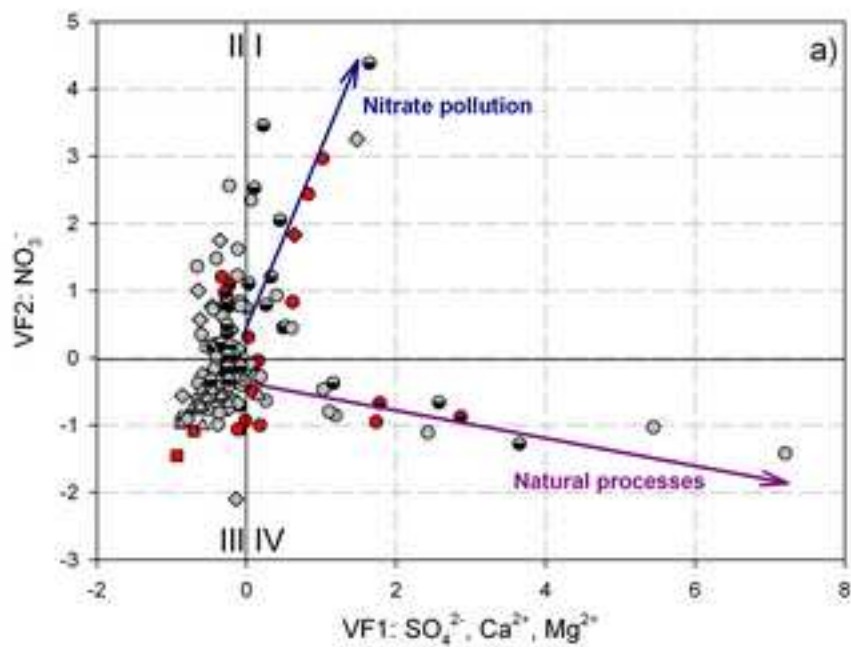


Figure 4
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