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

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

27 K^+, and Mg^{2+}). Moreover, positive linear relationships between nitrate and some ions are

28 found indicating the magnitude of the fertilization impact on groundwater hydrochemistry.

29 Nevertheless, the increasing concentration of specific ions is not only attributed to the manure

30 input, but to the enhancing effect of manure and slurry upon the biogeochemical processes

31 that control water-rock interactions. Such results raise awareness that such processes should

32 be evaluated in advance in order to assess adequate groundwater resources assessment.

33 **Highlights**

34 • The effects of nitrate pollution have been evaluated in five different aquifer types

35 • Statistical and multivariate analyses are used to identify groundwater changes

36 • Agricultural pollution modifies groundwater conditions and geochemical processes

37

38 **INTRODUCTION**

39 Nitrate occurrence and transport in aquifers have been widely studied since it is one of the

40 major threats in groundwater, and most aquifers in agricultural areas are affected by this

41 contaminant (Spalding and Exner, 1993; EEA, 2012). Most of the papers that focused on

42 nitrate pollution study, by means of hydrochemical and isotopic data, nitrate trends in

43 groundwater at different scales to identify potential sources of pollution and build-up

44 hydrogeochemical models to understand the behavior of nitrate polluted aquifers (for

45 instance, Burg and Heaton,1998; Hudak, 2000; Katz et al., 2004; Masetti et al., 2008; Vitòria

46 et al., 2008; Carbó et al., 2009; Kaown, et al., 2009; Menció et al., 2011; Boy-Roura et al.,

47 2013). However, agricultural pollution due to a long and continued application of organic

48 fertilizer (slurry and manure) may not only entail an increase on this ion in aquifers. On the

49 one hand, other substances present in manure also enter into the groundwater system, such as

50 ions, metals, emerging organic contaminants, or even microorganisms. On the other hand,

51 these substances interact with the subsurface environment, modifying groundwater

52 conditions, enhancing geochemical processes and even modifying groundwater communities

53 (Cho et al., 2000; Böhlke, 2002; Murray et al., 2010; Stein et al., 2010; Korbel and Hose,

54 2011; Lapworth et al., 2012; Korbel et al., 2013; Choi et al., 2013).

55 In this study, we look for the evidence of the changes that manure application exerts on the

56 major components concentrations by conducting an analysis of a large hydrochemical

57 database, including isotopic data, of nitrate polluted aquifers representative of several

58 geological environments. Our aim is to analyze whether manure and slurry application lead to

59 a loss of the hydrogeological fingerprint of the geological background, and whether the

60 resulting groundwater composition is only caused by mixing with manure lixiviates or by

61 changes in biogeochemical processes.

62 Manure applied as fertilizer has a complex chemical composition. For instance, Vitòria

63 (2004) analyzed its composition from several farms in Osona (Catalonia, NE Spain) and

64 reported that the concentration of some major inorganic components in pig manure, the most

65 used organic fertilizer in the studied areas in Catalonia (NE Spain), is notably larger than

66 their natural values in groundwater. This is the reason why its impact on groundwater

67 hydrochemistry must be evaluated to avoid misinterpretation of supposedly hydrochemical

68 natural data.

69 Samples for this study belong to four distinct regions in Catalonia, all of them classified as

70 Nitrate Vulnerable Zones (NVZs) as a result of the transposition of the Nitrate Directive

71 (ND) 91/676/EC. In fact, NVZs in Catalonia cover up to 40% of the total area, and half of

72 them show nitrate concentrations higher than 40 mg/L, affecting 17 out of the 53

73 groundwater bodies which are at risk of not meeting the European Water Framework

74 Directive goals (ACA, 2007; Boy-Roura, 2013). In this study, we analyze datasets from the

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 Ca^{2+}-HCO_3^- and Ca^{2+}-HCO_3^--Cl^- facies, tending to

84   evolve to Na^+-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 Ca^{2+}-

90   HCO_3^-, Ca^{2+}-Mg^{2+}-HCO_3^- or Ca^{2+}-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.

4

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 Ca^{2+}-HCO_3^- or Ca^{2+}-Mg^{2+}-HCO_3^- facies.

106

107 **METHODOLOGY**

108 Field surveys, in the studied datasets (Folch et al., 2011; Mencló et al., 2012; Puig et al.,

109 2013; Puig, 2014; Otero et al., 2009; Mencló 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 ±5%. Isotope δ-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 ±0.06‰ for $\delta^{18}O$ and ±0.7‰ for δD. Nitrate isotope notation is also expressed in terms of δ

120 (‰) relative to that of the international standards AIR (atmospheric N_2) for $\delta^{15}N$. Precision

121 (≡1σ) of the samples are ±0.3‰ and ±0.4‰, for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$, 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).

132

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

6

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 $\delta^{18}O$ 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 ($\delta^{15}N_{NO3}$). 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 $\delta^{15}N_{NO3}$. 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; Mencló 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 $\delta^{18}O$, 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 $\delta^{18}O$ (Table 1, Figure 2 and Figure 3).

225   •   VF4 is mainly associated to $\delta^{15}N_{NO3}$, 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 $\delta^{15}N_{NO3}$

228   values ($\delta^{15}N > 15‰$, 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 Na^+-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 $\delta^{18}O$ 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

10

247 volcanic rocks, present low VF2 values, consistent with the comparatively low pollution

248 levels in this aquifer type (Table 1).

249 Finally, when nitrate content (VF2) and nitrate attenuation (VF4) are plotted (Figure 3c),

250 samples with the highest nitrate concentration (with values exceeding 150 mg NO_3^-/L at VF2

251 scores > 1) are located in quadrants I and II; while quadrants I and IV include those samples

252 affected by natural attenuation (with $\delta^{15}N$>15‰). Samples of quadrant I and IV indicate that

253 attenuation processes are active independently of the nitrate concentration. Besides, in some

254 cases, nitrate content has been reduced to values lower than the health standard limits of 50

255 mg/L, as represented by the sample with negative scores of VF2. These nitrate attenuation

256 processes have been detected in all aquifers types.

257 Bivariate plots of selected ions against nitrate concentrations point out their linear increase

258 proportional to manure application. SO_4^{2-} and Ca^{2+} (both included in VF1) and Cl^-

259 (participating in VF2 and VF3) as major components illustrate this fact (Figure 4). Linear

260 regression equations are estimated for each aquifer lithology using all the available data,

261 despite their $\delta^{15}N_{NO3}$ value. Such regression equations prevail over two facts: 1) the inherent

262 variability of the manure chemical composition depending on its origin and storage before

263 application; and 2) the heterogeneity of soil processes, which are different, in type and

264 magnitude, depending on the soil nature and the crop type. Therefore, equations indicate the

265 rate of ion concentration changes with increasing nitrate content (slope); that is, the amount

266 of each ion that any unit of nitrate adds to groundwater whether as a direct input or as a result

267 of enhancing geochemical processes; and the expected value of the major component where

268 no fertilization occurs (y-intercept). Such linear increase is quite evident for these three ions,

269 and similar relationships occur for other major components.

270 Nevertheless, each geological environment show distinct responses to nitrate inputs. Water-

271 rock interaction in igneous and metamorphic rocks (group 1) will depend on the low

272 solubility of silicate minerals, and of other processes as cation exchange, which may

273 significantly alter the Ca^{2+}: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 mg NO_3^-/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 decreease;

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).

312

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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FIGURE CAPTIONS

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

445 **Figure 2.** Box plots of the main hydrochemical parameters according to the aquifer groups

446 and nitrate concentrations ranges: Low nitrate concentrations refer to values below 50 mg/L,

447 and high nitrate concentrations refer to values above 50 mg/L (see SI2 for details). Legend:

448 Boxes represent the 25 and 75 percentiles and the median; while a white line represents the

449 mean value. Bars define the 10 and 90% percentile, and dots refer to extreme values.

450 **Figure 3**. PCA scores distribution of the different samples, considering denitrification,

451 plotted according the lithological group and the $\delta^{15}N_{NO3}$, content: a) VF1 vs VF2, b) VF3 vs

452 VF2, and c) VF4 vs VF2.

453 **Figure 4.** Bivariate relationships of SO_4^{2-}, Ca^{2+} and Cl^- vs. NO_3^-. Linear regression equations

454 are calculated for all the samples of the group, disregarding their $\delta^{15}N$ value. *Legend*: red

455 circles, samples with $\delta^{15}N$ >15‰; black circles, samples with $\delta^{15}N$<15‰; white circles,

456 samples with $\delta^{15}N$ data not available.

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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 (µS/cm)	819±110	915±135	819±70	1124±65	841±72	1073±78	770±27	1070±64	623±21	779±31
pH	7.18±0.14	6.99±0.04	7.35±0.09	7.43±0.06	7.47±0.12	7.28±0.08	7.18±0.04	7.08±0.04	7.47±0.06	7.25±0.21
Eh (mV)	236.7±62.1	386.5±39.3	190.1±20.1	247.4±27.4	354.9±38.7	379.8±8.3	161.0±13.5	164.3±17.3	274.6±21.0	240.0±10.0
T (°C)	17.4±0.5	16.9±0.3	15.4±0.6	15.9±0.4	16.3±0.4	16.4±0.2	15.1±0.4	13.2±0.2	14.5±0.6	14.5±0.4
O_2 (mg/L)	1.5±0.6	3.9±1.4	4.0±0.6	4.0±0.5	3.7±1.1	5.2±0.5	4.6±0.6	4.4±0.4	8.0±0.6	7.6±1.3
HCO_3^- (mg/L)	368.1±59.6	346.9±40.0	418.3±15.4	388.0±13.0	355.1±34.4	360.7±13.5	411.9±18.6	407.4±13.1	284.8±13.0	341.7±39.0
Cl^- (mg/L)	101.0±24.7	99.2±42.8	42.4±6.7	94.9±10.4	86.1±15.1	91.8±11.9	16.0±1.6	73.3±12.4	16.1±2.2	30.7±10.4
SO_4^{2-} (mg/L)	35.9±5.7	57.2±8.6	132.4±46.4	164.3±32.1	68.4±16.8	98.1±12.4	43.5±5.4	184.6±34.6	48.0±6.5	41.4±8.2
NO_3^- (mg/L)	13.7±4.2	105.3±20.3	17.0±2.5	166.3±19.4	18.6±4.4	137.5±16.6	25.4±2.7	172.2±25.2	23.9±2.4	71.4±10.0
Na^+ (mg/L)	104.2±38.0	79.7±18.6	34.8±4.2	54.3±7.5	63.5±12.0	56.4±5.1	12.5±1.4	42.0±5.6	16.5±1.5	21.5±.9
K^+ (mg/L)	2.2±0.4	1.0±0.3	4.4±1.7	8.5±2.4	2.4±0.4	5.8±3.0	2.8±0.6	8.8±2.1	7.6±0.7	6.9±1.7
Ca^{2+} (mg/L)	82.6±14.0	127.5±21.5	132.6±16.2	185.7±10.1	110.7±12.7	166.3±9.7	135.8±7.1	196.0±10.8	87.2±4.5	89.5±8.4
Mg^{2+} (mg/L)	14.6±3.6	22.0±3.5	37.4±5.4	38.2±3.8	19.3±2.0	22.7±2.4	21.0±1.1	44.1±5.6	19.5±1.2	34.1±3.5

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Table 2. Loadings obtained in the second PCA, including $\delta^{15}N_{NO3}$, 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 (µS/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
$\delta^{18}O_{H2O}$ (‰)	-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>
$\delta^{15}N_{NO3}$ (‰)	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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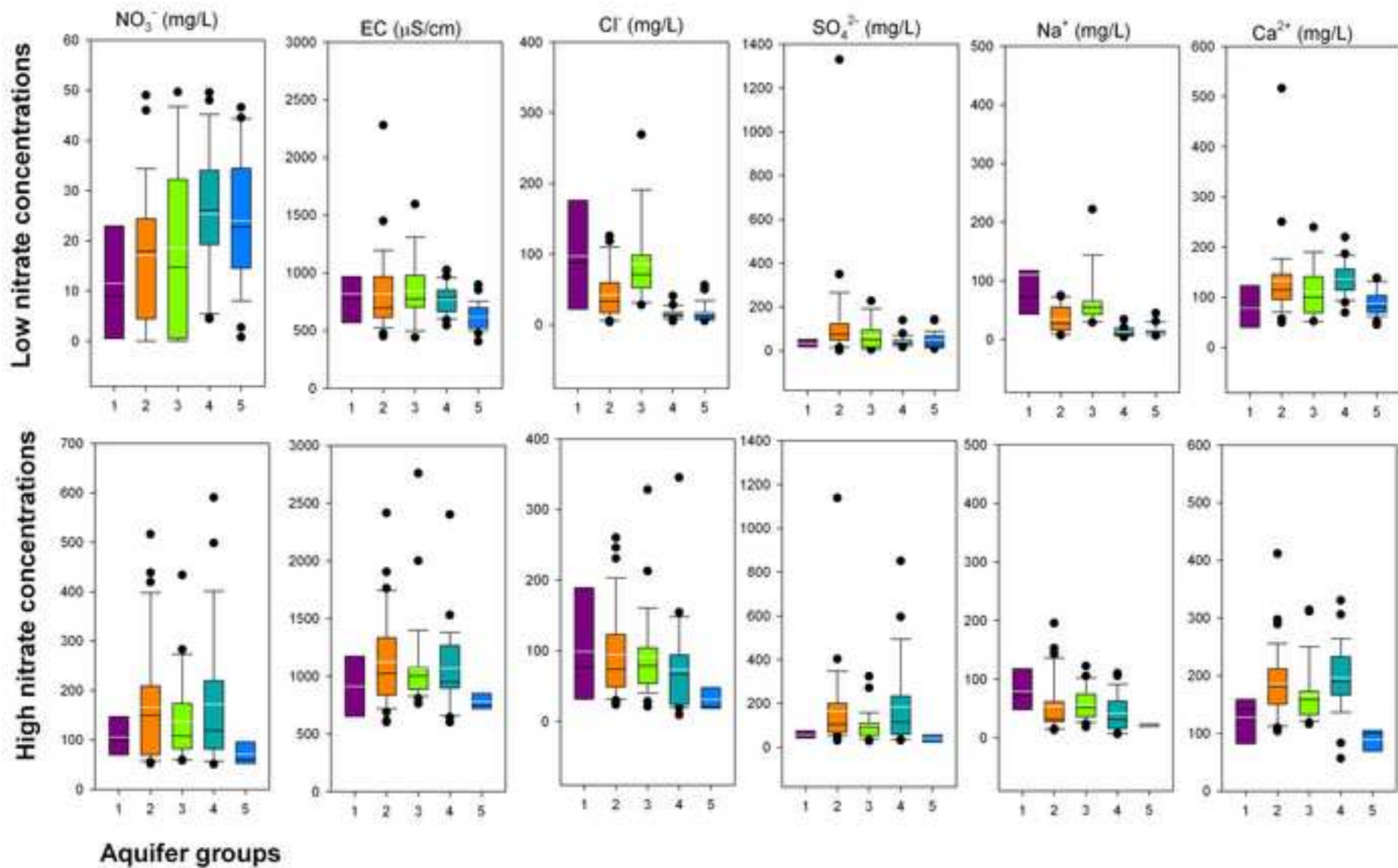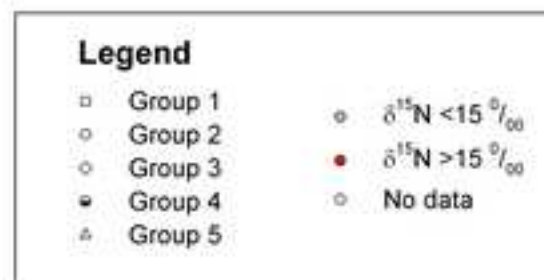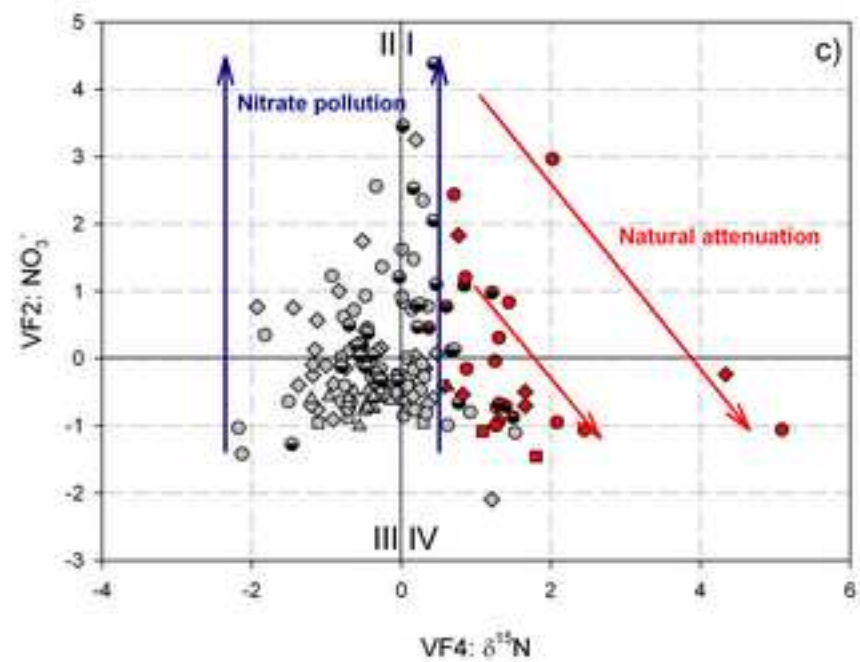**Figure 1**
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Lithology

- Igneous rocks (Paleozoic)
- Metamorphic rocks (Paleozoic)
- Sedimentary rocks (Mesozoic)
- Sedimentary rocks (Paleogene)
- Sedimentary materials (Neogene)
- Sedimentary materials (Quaternary)
- Volcanic materials

Sampling points

- $\delta^{15}N > 15$ ‰
- $\delta^{15}N < 15$ ‰
- Without $\delta^{15}N$ data
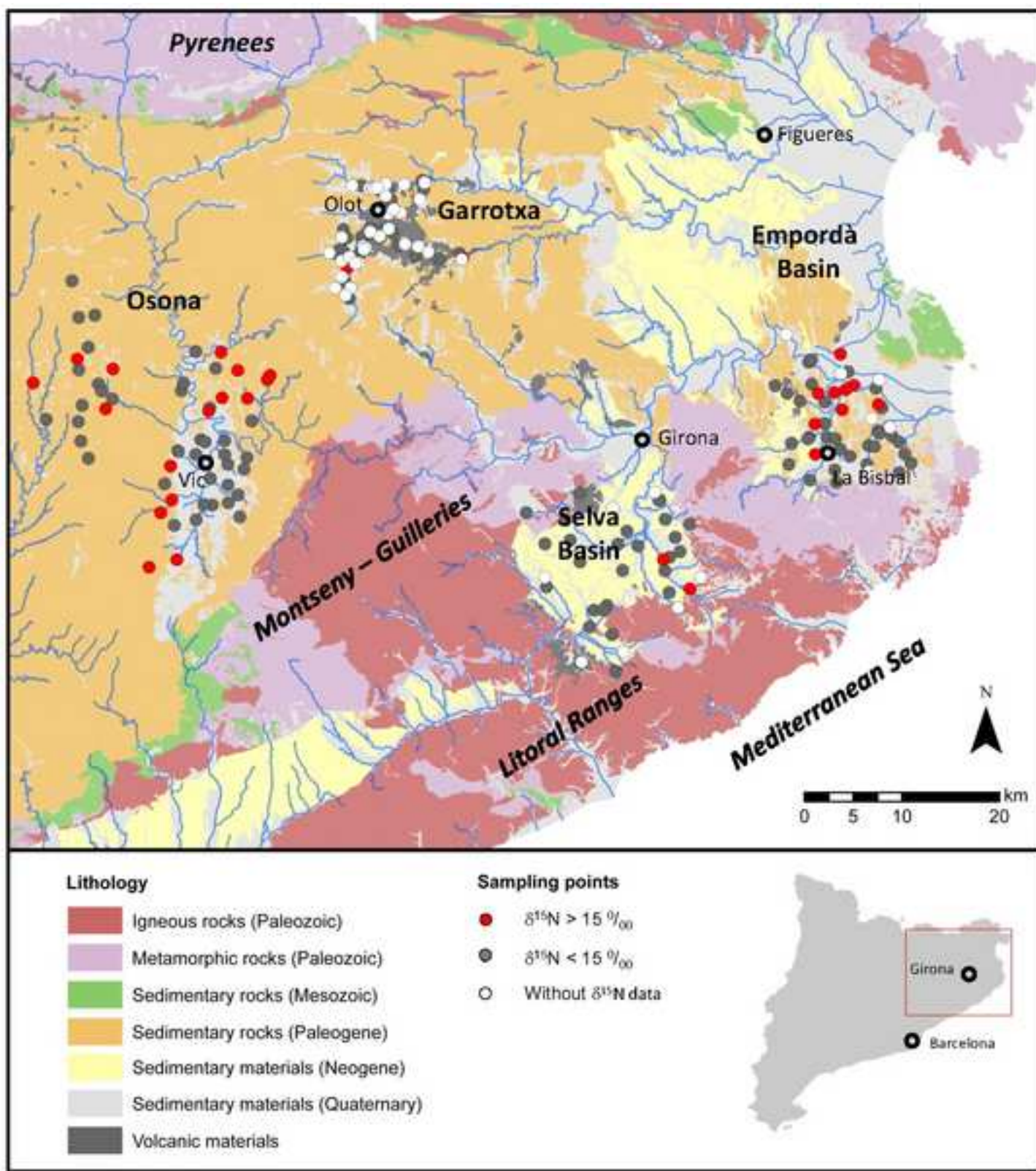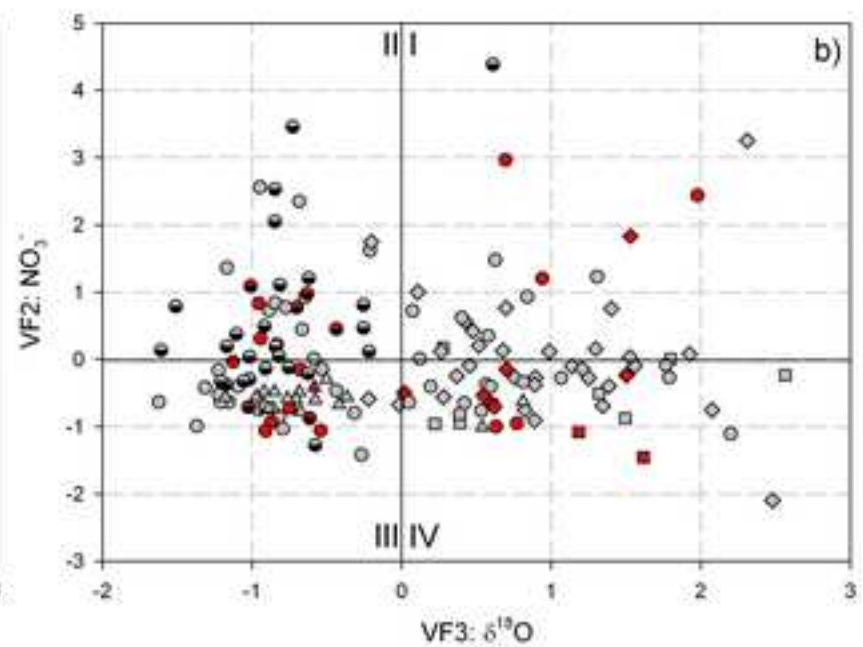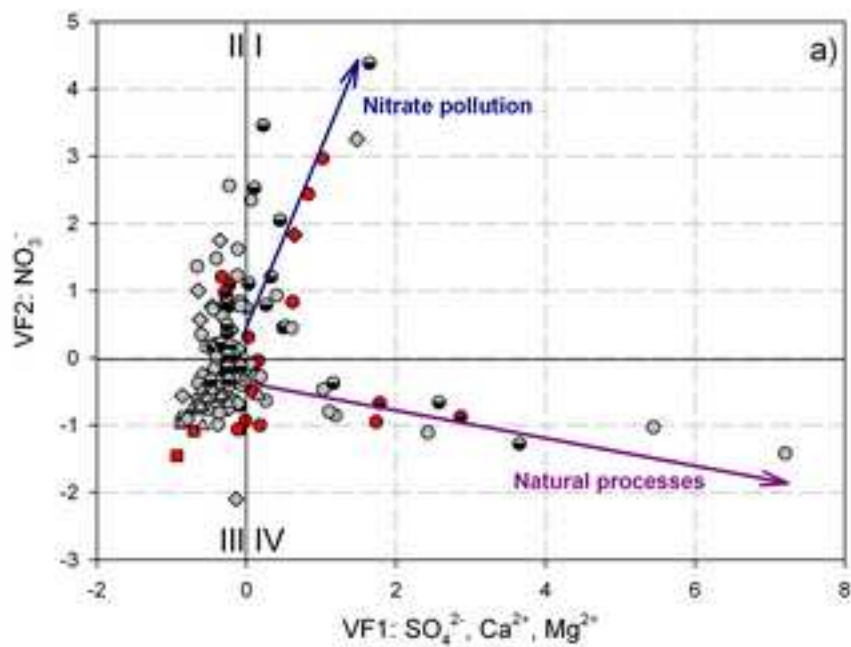
Figure 2

Figure 3
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Figure 4
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Figure 4