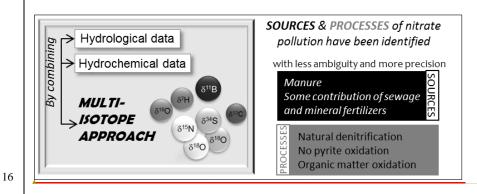


- δ^{15} N, δ^{18} O_{NO3} and δ^{11} B confirm pig manure as the main vector of NO₃-pollution.
- SO₄²⁻ and B isotopes indicate also contributions from sewage and mineral fertilizers.
- NO_3^- isotopes show that NO_3^- undergoes natural attenuation.
- SO_4^{2-} isotopes confirm that denitrification is not controlled by pyrite oxidation.
- The multi-isotope approach provides a unique and comprehensive approach that allows to characterise the origin of NO₃⁻ pollution as well as the processes involved.

- 1 Characterizing sources and natural attenuation of nitrate contamination in the
- 2 **Baix Ter aquifer system (<u>NE</u>Spain) using a multi-isotope approach**
- 4 Roger Puig^a, Albert Soler^a, David Widory^b, Josep Mas-Pla^{c, d}, Neus Otero^a and Cristina
 5 Domènech^a and Neus Otero^a
- 6

- 7 ^aGrup de Mineralogia Aplicada i Geoquímica de Fluids, Dept. de Mineralogia, Petrologia i
- 8 Geologia Aplicada, Facultat de GeologiaCiències de la Terra, Universitat de Barcelona (UB), c/
- 9 Martí i Franquès s/n, 08028 Barcelona, Spain.
- ^bDépartement des Sciences de la Terre et de l'Atmosphère, Geotop/UQAM, Montréal, Canada.
- ¹¹ ^cGrup de Geologia Aplicada i Ambiental, Centre de Geologia i Cartografia Ambiental, Dept. de
- 12 Ciències Ambientals, Universitat de Girona, 17003 Girona, Spain.
- 13 ^dCatalan Institute for Water Research, c/ Emili Grahit 101, 17003 Girona, Spain.
- 14 **Corresponfing author:** Cristina Domenech (cristina.domenech@ub.edu)
- 15 Graphical abstract



Formatted: Font: 12 pt, Bold

	MULTI-ISOTOPE APPROACH
	Hydrological data B ² H Hydrochemical data
	δ ¹¹ B δ ¹⁸ O _{δ³⁴S} δ ¹³ C
	Sources
17	Less ambiguity and more precision. Better water management policies
18 19	Highlights
20	We applied a multi-isotope approach to characterize nitrate contamination in a large-
21	scale polluted aquifer system.
22	- δ^{15} N, δ^{18} O _{NO3} and δ^{11} B confirm pig manure as the main vector of NO ₃ -
23	pollution.
24	- SO_4^{2-} and B isotopes indicate also contributions from sewage and mineral
25	fertilizers.
26	- NO_3^- isotopes show that NO_3^- undergoes natural attenuation.
27	<u>-</u> SO ₄ ²⁻ isotopes reveal that confirm that denitrification is not controlled by pyrite
28	oxidation.
29	- The multi-isotope approach provides a unique and comprehensive approach that
30	allows to characterise the origin of NO_3^- pollution as well as the processes
31 32	involved.
33	Abstract
34	Nitrate pollution is a widespread issue affecting global water resources with
35	significant economic and health effects. Knowledge of both the corresponding pollution
36	sources and of processes naturally attenuating them is thus of crucial importance in
37	assessing water management policies and the impact of anthropogenic activities. In this
38	study, an approach combining hydrodynamic, hydrochemical and multi-isotope
39	systematics (8 isotopes) is used to characterise the sources of nitrate pollution and
40	potential natural attenuation processes in a polluted basin of NE Spain. $\delta^2 H$ and $\delta^{18} O$

41	isotopes were used to further characterize the sources of recharge of the aquifers.
42	Results show that NO ₃ ⁻ is not homogeneously distributed and presents a large range of
43	concentrations, from no NO ₃ ⁻ to up to 480 mg L ⁻¹ . δ^{15} N and δ^{18} O of dissolved NO ₃ ⁻
44	identified manure as the main source of nitrate, although sewage and mineral fertilizers
45	can also be isotopically detected using boron isotopes ($\delta^{11}B$) and $\delta^{34}S$ and $\delta^{18}O$ of
46	dissolved sulphate, respectively. The multi-isotope approach proved that natural
47	denitrification is occurring, especially in near-river environments or in areas
48	hydrologically related to fault zones. δ^{34} S and δ^{18} O indicated that denitrification is not
49	driven by pyrite oxidation but rather by the oxidation of organic matter. This could not
50	be confirmed by the study of $\delta^{13}C_{HCO3}$ that was buffered by the entanglement of other
51	processes and sources.
52	Keywords
53	Stable isotopes, nitrate contamination, boron, denitrification, groundwater, manure
54	
54 55	1. Introduction
	1. Introduction <u>Nitrate (NO₃⁻) contamination of groundwater is a problem affecting groundwater</u>
55	
55 56	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater
55 56 57	<u>Nitrate (NO₃⁻) contamination of groundwater is a problem affecting groundwater</u> <u>quality worldwide (Xu et al., 2016 and references therein)</u> that has proved to affect
55 56 57 58	<u>Nitrate (NO₃⁻) contamination of groundwater is a problem affecting groundwater</u> <u>quality worldwide (Xu et al., 2016 and references therein) that has proved to affect</u> <u>human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable</u>
55 56 57 58 59	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of
55 56 57 58 59 60	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of NO_3^- inputs and the enhancement of attenuation processes in groundwater.
55 56 57 58 59 60 61	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of NO ₃ ⁻ inputs and the enhancement of attenuation processes in groundwater. However, no decreasing trends in average European nitrate concentration in
 55 56 57 58 59 60 61 62 	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of NO ₃ ⁻ inputs and the enhancement of attenuation processes in groundwater. However, no decreasing trends in average European nitrate concentration in groundwater have been observed during the last 15 years (EEA, 2015). Thus,
 55 56 57 58 59 60 61 62 63 	Nitrate (NO ₃ ⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of NO ₃ ⁻ inputs and the enhancement of attenuation processes in groundwater. However, no decreasing trends in average European nitrate concentration in groundwater have been observed during the last 15 years (EEA, 2015). Thus, Groundwater contamination arising from long-standing agricultural practices is a global

66	$\frac{\text{conmitrateNO_3}}{\text{concentrations}}$ in groundwater $\frac{\text{casily}}{\text{coften}}$ exceeds the 50 mg L ⁻¹ legal
67	threshold-guideline value set for drinking water (EC, 1998). NO ₃ is currently one of the
68	According to the European Environmental Agency (EEA, 2015), the European average
69	concentration of nitrate in groundwater in 2012 was 19.1 mg L^{-1} , equivalent to the
70	previous average of 2000. In Spain, corresponding mean values are significantly higher:
71	32.3 mg L^{-1} in 2000 and 34.5 mg L^{-1} in 2012. NO ₃ ⁻ is thus, one of the main
72	contaminants that may hinder the achievementing of the goals of the Water Framework
73	(EC, 2000) and of the European Groundwater (EC, 2006) directives. This arises the
74	need for a better knowledge on the overall nitrogen, including nitrate species cycle in
75	surface water and groundwater.
76	Because of this, significant efforts are done to minimise nitrate concentration in
77	groundwater either by reducing its incorporation and/or by enhancing its attenuation
78	(Archna et al. 2012).
79	Nitrogen is mainly itrate contamination mainly arises from the biological
80	transformation of the nitrogen incorporated into the soil as a nutrient through mineral
81	fertilizers or manure, each of these sources accounting for. Each of these two sources
82	accounts from nearly 50% of all-the N input into the European agricultural soils (EEA,
83	2012). However, other minor \underline{N} sources have been reported such as the leakage of
84	sewage from sewer networks in urban environments (Barroso et al. 2015; Aravena and
85	Mayer, 2010; <u>Barroso et al., 2015;</u> Sacchi et al., 2013; Vane et al., 2010) have been
86	reported for groundwater.
87	Once in the soil, nitrogen is transformed Nitrogen transformation through may
88	occur through different microbially mediated redox reactions (nitrogen fixation,
89	nitrification, denitrification, dissimilatory NO_3^- reduction to ammonium, anammox;
90	Borch et al., 2010). Nitrification, represents the oxidation of nitrogen (as-under the form

91	of ammonia) into nitrate. It, frequently occurs in the unsaturated zone given the
92	availability of where oxygen is available, and explains why most of the nitrogen that
93	reaches groundwater appears as NO ₃ ⁻ . <u>Denitrification is </u> F the transformation of nitrate
94	into $N_2(g)$ -and it. It is called denitrification and is considered the main natural process
95	attenuating nitrate concentration in groundwater. This requires The required conditions
96	for natural denitrification include 1) the presence of denitrifying bacteria and electron
97	donors (organic carbon, reduced sulphur and/or reduced iron), -2) abundant presence of
98	NO ₃ ⁻ and 3) an anaerobic environment (Koba et al., 1997; dissolved oxygen
99	concentrations below 2 mg L ⁻⁺ ; Rivett et al., 2008) or an anaerobic microsite within an
100	otherwise oxygenated water body (Koba et al., 1997). Denitrification can be
101	heterotrophic if linked to the oxidation of an organic compound (eq.1) or autotrophic, if
102	linked to the oxidation of an inorganic compound, such as iron sulphide (eq.2).
103	$4NO_3^- + 5CH_2O \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$ (1)
104	$14NO_{3}^{-} + 5FeS_{2} + 4H^{+} \rightarrow 7N_{2} + 10SO_{4}^{2-} + 5Fe^{2+} + 2H_{2}O$ (2)
105	
	Dilution and dispersion are other processes that can Similar to natural attenuation,
106	Dilution and dispersion are other processes that can Similar to natural attenuation, the processes of dilution and dispersion can also result in a decrease of groundwater
106	the processes of dilution and dispersion can also result in a decrease of groundwater
106 107	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to - However, only-natural attenuation, they do not
106 107 108	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to - However, only natural attenuation, they do not lead to leads to the mass-reduction of the contaminant within the aquifer making it the
106 107 108 109	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to - However, only-natural attenuation, they do not lead to leads to the mass-reduction of the contaminant within the aquifer making it the most interesting process to achieve water quality management goals.
106 107 108 109 110	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to - However, only-natural attenuation, they do not lead to -leads to the mass-reduction of the contaminant within the aquifer making it the most interesting process to achieve water quality management goals. Knowledge of both the sources of nitrogen contamination and the processes
106 107 108 109 110 111	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to . However, only natural attenuation; they do not lead to leads to the mass-reduction of the contaminant within the aquifer making it the most interesting process to achieve water quality management goals. Knowledge of both the sources of nitrogen contamination and the processes affecting nitrogen once in the aquifer is thus of the utmost importance to better design
106 107 108 109 110 111 112	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to -However, only-natural attenuation, they do not lead to -leads to the mass-reduction of the contaminant within the aquifer making it the most interesting process to achieve water quality management goals. Knowledge of both the sources of nitrogen contamination and the processes affecting nitrogen once in the aquifer is thus of the utmost importance to better design strategies to ultimately decrease nitrate pollution. The study of the isotope composition
106 107 108 109 110 111 112 113	the processes of dilution and dispersion can also result in a decrease of groundwater nitrate concentration, but contrarily to . However, only natural attenuation; they do not lead to leads to the mass-reduction of the contaminant within the aquifer making it the most interesting process to achieve water quality management goals. Knowledge of both the sources of nitrogen contamination and the processes affecting nitrogen once in the aquifer is thus of the utmost importance to better design strategies to ultimately decrease nitrate pollution. The study of the isotope composition of nitrogen compounds has proved to be a viable tool to tackle both issues (e.g. Amiri et

116	residual nitrate leading to an causing an enrichment in its heavy isotopes ¹⁵ N and ¹⁸ O
117	(Aravena and Robertson, 1998; Fukada et al., 2003; Kendall et al., 2007; Mariotti et al.,
118	1988). The study of the δ^{15} N and δ^{18} O isotope compositions and nitrate concentrations
119	(eq. 3 and 4) allow to determine the corresponding . Residual δ^{15} N and δ^{18} O are related
120	to the sources initial isotope compositions and to the nitrate concentration according to
121	equations 3 and 4, respectively (Böttcher et al., 1990; Fukada et al., 2003; Mariotti et
122	al., 1981), where c is the isotopic enrichment factor (c), used to characterise the
123	extension of the attenuation processes depending on the aquifer characteristics (Böttcher
124	et al., 1990; Fukada et al., 2003; Mariotti et al., 1981). Also, as the initial NO3 ⁻ isotope
125	compositions differ between the different nitrate sources (inorganic fertilizers, manure,
126	soil,), the δ^{15} N and δ^{18} O compositions of nitrate have been used to identify its origin
127	in groundwater (Aravena et al., 1993; Aravena and Mayer, 2010; Clark and Fritz, 1997;
128	Kendall et al., 2007; Panno et al., 2001).
129	$\delta^{15} N_{residual} = \delta^{15} N_{initial} + \varepsilon_N \ln \left([NO_3]_{residual} / [NO_3]_{initial} \right) $ (3)
130	$\delta^{18}O_{\text{residual}} = \delta^{18}O_{\text{initial}} + \varepsilon_0 \ln \left([NO_3]_{\text{residual}} / [NO_3]_{\text{initial}} \right) $ (4)
131	Moreover, as the initial δ^{15} N and δ^{18} O composition differs within the different
132	nitrate sources (inorganic fertilizers, manure, soil organic), the isotopic composition
133	of nitrate has been proved to be a useful tool to distinguish between them (e.g. Curt et
134	al., 2004; Kendall et al., 2007).
135	This two-fold information the isotope composition of nitrate (δ^{15} N and δ^{18} O)
136	provides, 1) the origin of nitrate and 2) the occurrence (and extension) of natural
137	attenuation and other processes affecting nitrogen compounds, reveals the importance of
138	using isotopic tools in assessing nitrate pollution in groundwater (Aravena et al., 1993;
139	Aravena and Mayer, 2010; Clark and Fritz, 1997; Kendall, 1998; Kendall et al. 2007;
140	Panno et al., 2001).
l	

141	However, in areas characterized by a complex groundwater flow systems and
142	exposed to multiple potential sources of nitrogen, the use of the sole δ^{15} N and δ^{18} O of
143	<u>NO₃ and nitrate concentrations may result in not it is usually difficult to c</u> onclusively
144	results. identify the main origin and processes controlling the nitrogen budget based on
145	the sole study of δ^{15} N and δ^{18} O of NO ₃ ⁻ .
146	To overcome this difficulty, as the redox transformations affecting nitrate also affect
147	the electron donor, some authors have coupled $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- data with the
148	isotope composition of the electron donors or with other types of hydrochemical data,
149	such as conservative elements (Xu et al., 2016). Some authors combined chloride
150	concentration (a conservative element) with $\delta^{15}N$ and $\delta^{18}O$ of NO ₃ ⁻ to identify nitrate
151	sources and transformation processes (Silva et al. 2002, Vitòria et al. 2008). Some
152	others used the δ^{34} S and δ^{18} O of sulphate or $\delta^{13}C_{HCO3}$ to evaluate if sulphide or organic
153	matter oxidation processes could be linked to denitrification processes (Aravena and
154	Robertson, 1998; Otero et al., 2009; Rock and Mayer, 2002; Saccon et al., 2013; Vitòria
155	<u>et al. 2005, 2008).</u>
156	several studies proposed a multi-isotope approach coupling hydrochemical data and
157	δ^{15} N and δ^{18} O of NO ₃ ⁻ with the isotope compositions of ions involved in the
158	denitrification reactions (eq. 1 and 2): $\delta^{34}S$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{HCO3}$ (Aravena and
159	Robertson, 1998; Cravotta, 1997; Otero et al., 2009; Rock and Mayer, 2002; Saccon et
160	al., 2013; Vitòria, 2004; Vitòria et al., 2005, 2008), obtaining satisfactorily results.
161	Moreover, in the last decade, some studies have also used the isotope composition
162	of boron ($\delta^{11}B$) in combination with the $\delta^{15}N$ and $\delta^{18}O$ of NO ₃ ⁻ to trace the origin of
163	NO ₃ ⁻ in water (Delconte et al., 2014; Komor, 1997; Saccon et al., 2013; Seiler, 2005;
164	Widory et al., 2004, 2005, and 2013). B is usually found in natural ground- and surface
165	water as a minor constituent ($<0.05 \text{ mg B } \text{L}^{-1}$) whereas contaminant sources are

166	enriched in B (>0.1 mg B L^{-1} ; Tirez et al., 2010). Besides the fact that groundwater
167	affected by anthropogenic activities may present elevated B contents (Vengosh et al.,
168	1994), δ^{11} B values are significantly discriminated between manure and wastewater. As
169	for nitrate isotopic composition, $\delta^{11}B$ of dissolved B can be modified by different
170	processes. However, the processes that can shift B isotopic composition are aquifer
171	matrix interaction (dissolution of B-bearing silicates) and adsorption-desorption
172	interactions with clay minerals, iron and aluminium oxide surfaces, and/or organic
173	matter (Yingkai and Lan, 2001). No effects on $\delta^{11}B$ composition are caused by
174	volatilization and oxidation-reduction reactions (Bassett et al., 1995). Thus, the
175	incorporation of δ^{11} B in the multi-isotope approach of nitrate polluted areas may be
176	useful for a better identification of NO_3^- sources (manure or sewage), especially in
177	semirural zones where agricultural and farming practices cohabitate with industrial and
178	urban activities.
179	However, to our knowledge no study trying to combine these chemical/isotope
179 180	<u>However, to our knowledge no study</u> trying to combine these chemical/isotope approaches has ever been reported so far. Here, we aim at assessing the added value
180	approaches has ever been reported so far. Here, we aim at assessing the added value
180 181	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotope parameter approach in which, besides the classical δ^{15} N and
180 181 182	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotope parameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with hydrochemical and hydrodynamic data (e.g. Cl ⁻)
180 181 182 183	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi- <u>isotope</u> parameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with <u>hydrochemical and hydrodynamic data (e.g. Cl</u> concentration), δ^{2} H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of
180 181 182 183 184	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotopeparameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with hydrochemical and hydrodynamic data (e.g. Cl ⁻ concentration), δ^{2} H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO ₃ ⁻ and δ^{11} B of dissolved B are used simultaneously to both identify both-the
180 181 182 183 184 185	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotopeparameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with hydrochemical and hydrodynamic data (e.g. CI concentration), δ^{2} H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO ₃ ⁻ and δ^{11} B of dissolved B are used simultaneously to both identify both-the sources and the natural attenuation processes of nitrate pollution from samples from
180 181 182 183 184 185 186	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotopeparameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with hydrochemical and hydrodynamic data (e.g. Cl ⁻ concentration), δ^2 H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO ₃ ⁻ and δ^{11} B of dissolved B are used simultaneously to both identify both the sources and the natural attenuation processes of nitrate pollution from samples from exploitation wells in an alluvial aquifer system contamination and to characterise
180 181 182 183 184 185 186 187	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotopeparameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ , combined with hydrochemical and hydrodynamic data (e.g. Cl ⁻ concentration), δ^{2} H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO ₃ ⁻ and δ^{11} B of dissolved B are used simultaneously to both identify both the sources and the natural attenuation processes of nitrate pollution from samples from exploitation wells in an alluvial aquifer system contamination and to characterise processes affecting the nitrate budget of a given watershed. The proposed multi-isotope
180 181 182 183 184 185 186 187 188	approaches has ever been reported so far. Here, we aim at assessing the added value validity of a multi-isotopeparameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO ₃ ⁻ , combined with hydrochemical and hydrodynamic data (e.g. CI concentration), δ^{2} H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO ₃ ⁻ and δ^{11} B of dissolved B are used simultaneously to both identify both-the sources and the natural attenuation processes of nitrate pollution from samples from exploitation wells in an alluvial aquifer system contamination and to characterise processes affecting the nitrate budget of a given watershed. The proposed multi-isotope approach includes the simultaneous study of eight isotopes systematics: δ^{2} H and δ^{18} O of

Spain), declared vulnerable to NO₃⁻ pollution in 1998 by the local government 191 following the 91/676/EC European Nitrate Directive (EC, 1991). NO₃⁻ contents in 192 groundwater exceeds the 50 mg $NO_3^{-}L^{-1}$ threshold (ACA, 2007) due to the large 193 amount of fertilizers used by local agriculture (Mas-Pla et al., 1998; Montaner et al. 194 195 2010) and pig raising practices that started in the 80's and intensified during the last decades (ACA, 2007; EEA, 1999). This aquifer is subjected to several anthropogenic 196 197 pressures such as additional nitrate sources or groundwater exploitation that increases 198 the complexity of the aquifer behaviour.

199

The assessment of the impact and occurrence of natural attenuation processes is of the utmost importance in the design of management strategies for groundwater quality 200 201 policies.

2. Study area 202

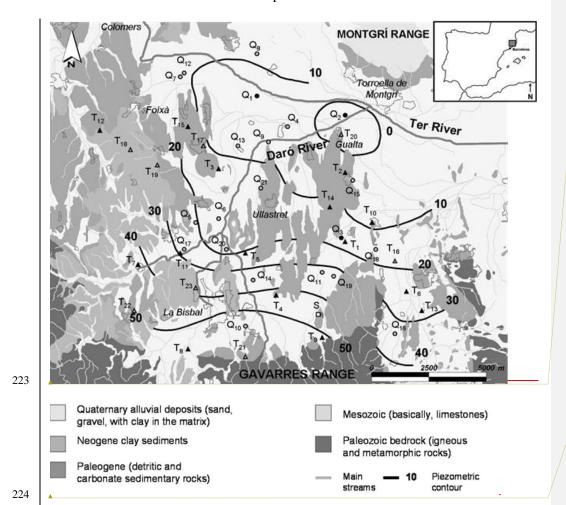
203 The Baix Ter basin is located in the Baix Empordà tectonic basin (NE Catalonia, Spain) (Fig. 1). The study zone encompasses a 200 km² area characterized by the Ter 204 205 River alluvial plain delimited by the Montgrí Range to the north (Mesozoic limestone 206 formations) and by the Gavarres Range to the south (Paleozoic igneous and 207 metamorphic rocks) that turns into a fluvio-deltaic environment in its eastern margin. 208 The foothills of the Gavarres Range, as well as the basin basement present Paleogene 209 sedimentary materials (sandstone and limestone formations) that are severely affected by fractures (Mas-Pla and Vilanova, 2001). 210 211 The Baix Empordà basin was formed during the distensive period of the Alpine orogenesis. Detritic, fine-grained and silty formations were sedimented during the 212

213 Neogene. The Quaternary fluvio-deltaic deposits originated from the Ter River as well

214 as from some minor tributaries from the Gavarres Range (i.e., Daró River, Fig. 1). They

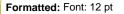
constitute the main aquifers of the area, and lay on the Neogene sediments in the 215

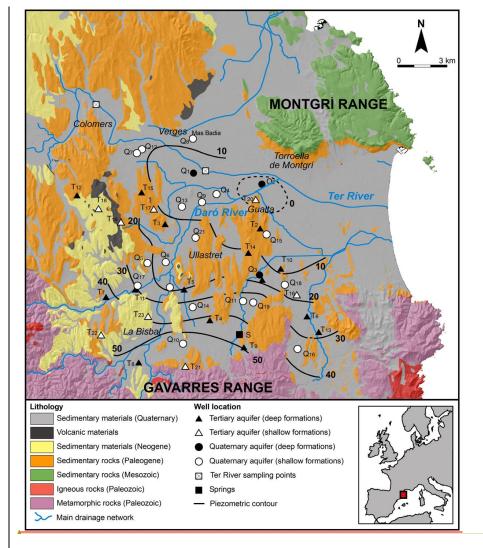
western area, and on the Paleogene in the eastern part of the basin. Fluvial deposits
reach a maximum depth of 50-60 m in the central part of the basin and are constituted
by three main distinguishable units according to the Holocene sedimentary sequence
(Montaner et al. 2010): a deep level formed by alluvial coarse detritic material, gravel
and sand; an intermediate level, formed by sandy lenticular bodies in a silty-sandy level;
and a shallow level, mainly sandy formed by the present prograding alluvial deposits
that transform into marsh and coastal deposits near the coast line.



Formatted: Font: 12 pt

Formatted: Font: 12 pt





226	Figure 1. Geological map of the Baix Ter basin, sampling point locations labelled
227	according to the hydrogeological formation where they are located. Potentiometric
228	contour lines of the unconfined aquifer, mainly in the shallow Quaternary formations,
229	correspond to the August 2004 survey. Dashed line represents the zero elevation
230	potentiometric level in the deep quaternary formations (mainly leaky aquifers) affected
231	by intensive withdrawal rates in the central area of the basin. Geology from ICGC
232	(http:// www.icgc.cat).Figure 1. Baix Ter basin map showing the geology and sampling
233	points, labelled according to their hydrogeological formation (round and triangle shapes

distinguish between Quaternary and Tertiary aquifers, respectively, and light and bold
 points, between shallow and deep formations, respectively; square refers to the sampled
 spring). Potentiometric contour lines correspond to the water table measurements of the
 Quaternary unit (August 2004).

238

Because of this lithological diversity, three distinct aquifer units are differentiated, 239 from bottom to top: a leaky aquifer formed by the deeper coarse sediment layer, a leaky 240 241 aquifer formed by the intermediate sandy layer, and an upper unconfined aquifer formed 242 by the prograding deposits. All of them present significant lateral variations, especially the upper aquifer that reflects the fluvio-deltaic, marsh and coastal areas presently 243 occurring in the plain. These aquifer units are separated by loamy layers that constitute 244 245 low permeability units that act as aquitards. Nevertheless, all three aquifer layers overlap in the westernmost part of the area, between Colomers and Verges. 246 247 According to Montaner et al. (2010) these aquifers are mainly recharged by local precipitation, seasonal contribution from the Ter and Daró rivers (whether natural or 248 249 induced by pumping), and by irrigation returns. Moreover, igneous and metamorphic 250 rocks at the Gavarres Range act as regional recharge areas that discharge into the fluvio-251 deltaic Quaternary aquifers through the preferential upward vertical flow paths of the limestone and carbonate Paleogene aquifers and, more importantly, through the 252 fractures that affect them (Vilanova and Mas Pla, 2004; Vilanova et al., 2008). 253 Potentiometric, hydrochemical and isotope data indicate that these different aquifers are 254 hydraulically connected (Vilanova, 2004Vilanova et al., 2008). 255 256 Potentiometric maps reveal an influent (losing stream) behaviour of the Ter River in 257 its western reach, between Colomers and Verges, and an effluent (gaining stream)

behaviour of the Ter and Daró rivers downstream of Verges down to the coast line.

259	However, intense groundwater withdrawal from these aquifers started in the 60's with
260	the agricultural and touristic development of the area that modified the natural flow
261	field causing a noticeable depression cone in the centre of the formation, between the
262	villages of Gualta and Torroella de Montgrí (Fig. 1). This cone creates a downward
263	flow from the upper unconfined aquifer, also capturing the Ter River discharge, which
264	recharges the supply wells located in the lower aquifer levels. The total groundwater
265	abstraction is around 21 hm^3/yr , from which 62% are for domestic use (including the
266	touristic season), 36% for agriculture activities and 2% for the industry (ACA, 2007).
267	The Baix Ter basin area supports rural agriculture and livestock activities, industrial
268	activities and several small to medium-sized urban areas that drastically increase their
269	population during summer due to their intense touristic activity. About 60% of the
270	surface is covered by herbaceous dry-farmed and irrigated crops (mainly maize,
271	sunflower and rice), 20% by forest and pasture and 7% by fruit growing (ACA, 2007).
272	The total nitrogen produced by livestock in the study zone is around 500 tons of N
273	year ⁻¹ . 60% of this amount are from intensive pig rising (460 pigs/km ² ; 50 m ³ ha ⁻¹ year ⁻¹
274	of pig manure are applied onto maize crops; ACA, 2007). However, leakage from
275	manure ponds or inappropriate spillages may also contribute to the increase of nitrogen,
276	which is unassimilated by crops and incorporated into the saturated zone, ultimately
277	raising NO_3^- concentrations in the groundwater. The "La Bisbal" water treatment plant
278	discharges downstream of Daró River and produces mud that is eventually applied onto
279	the fields, although some corrective measures were adopted to avoid wastewater spills.
280	3. Methodology
281	3.1. Sampling
282	Two sampling campaigns were conducted in the right bank alluvial plain of the

Baix Ter basin in January 2004 (24 wells) and in August 2004 (40 wells) to cover both

the wet season with fertilization and growing of dry land cereals and the dry season with cultivation of spring cereals, respectively.

286 All samples were taken from private wells supplied by the shallow Quaternary hydrogeological formation and the upper unconfined aquifer (Q_S) , in the deep 287 Quaternary formation and the lower unconfined aquifers (Q_D) , and in the shallow (T_S) 288 289 and deep (T_D) Tertiary formations located in the Paleogene materials (Fig.1). Most of 290 the locations were sampled during both campaigns. 291 After measuring groundwater hydraulic head, wells were pumped until the water Eh 292 stabilized. Then, temperature, pH and electrical conductivity (EC) were measured in situ and groundwater samples were collected in bottles that were previously rinsed several 293 294 times with groundwater. Samples were stored at 4°C in a dark environment before 295 analysis.

3.2. Analytical techniques

297 Temperature, pH, EC and Eh were measured using a flow cell to avoid contact with the atmosphere. Aqueous concentrations of chloride, nitrite, nitrate and sulphate were 298 299 determined by high-performance liquid chromatography (HPLC), HCO₃⁻ aqueous 300 concentration by volumetric titration, and total aqueous concentration of Na, K, Ca, Mg, 301 Fe, Mn and B by inductive-coupled plasma optical emission spectrometry (ICP-OES). 302 Ammonia aqueous concentration was determined by colorimetry (flow injection analysis), and total organic C (TOC) concentration by the organic matter combustion 303 304 method. All these analyses were done at the Centres Científics i Tecnològics of the 305 Universitat de Barcelona (CCiT-UB). δ^2 H and δ^{18} O of water were measured using the H₂ and CO₂ equilibration 306 techniques respectively. H and O isotope compositions were measured by DI-IRMS on 307

a Delta S Finnigan Mat. δ^{15} N and δ^{18} O of dissolved NO₃⁻ were measured using the

309	AgNO ₃ method (modified from Silva et al. (2000)) with an Elemental Analyser (Carlo
310	Erba 1108) coupled with an Isochrom Continuous Flow IRMS in the case of $\delta^{15}N$ and
311	with a Thermo-Chemical Elemental Analyser (TC/EA Thermo-Quest Finnigan) coupled
312	with a Delta C Finnigan Mat IRMS in the case of δ^{18} O (duplicate analyses). To measure
313	$\delta^{34}S$ and $\delta^{18}O$ of SO4 $^{2\text{-}},$ aqueous sulphate was precipitated as BaSO4 by acidifying the
314	sample with HCl, boiling it, and adding an excess of BaCl ₂ ·2H ₂ O. δ^{34} S was measured
315	using an Elemental Analyser (Carlo Erba 1108) coupled with a Delta C Finnigan Mat,
316	while $\delta^{18}O$ was measured with the same methodology (TC/EA-IRMS) as $\delta^{18}O$ of
317	nitrate. In order to measure δ^{11} B, sample volume was determined to ultimately yield 6 to
318	10 μ g of B. Samples then underwent a two-step chemical purification using Amberlite
319	IRA-743 selective resin (method adapted from Gaillardet and Allègre (1995)). First, the
320	sample (pH~7) was loaded on a Teflon $PFA^{(B)}$ column filled with a 1 ml resin,
321	previously cleaned with ultrapure water and 2N ultrapure NaOH. After cleaning again
322	the resin with water and NaOH, the purified B was collected with 15 ml of sub-boiled
323	HCl 2N. After neutralisation of the HCl by Superpur NH ₄ OH (20%), the purified B was
324	loaded again on a small 100 ml resin Teflon PFA® column. B was collected with 2 ml
325	of HCl 2N. An aliquot corresponding to 2 mg of B was then evaporated below 70° C
326	with mannitol $(C_6H_8(OH)_6)$ in order to avoid B loss during evaporation (Ishikawa and
327	Nakamura,1990). The dry sample was loaded onto a tantalum (Ta) single filament with
328	graphite (C), mannitol and caesium (Cs). $\delta^{11}B$ was determined on the Cs ₂ BO ²⁺ ion
329	(Spivack and Edmond, 1986) by negative-ion Thermal-Ionization Mass Spectrometry
330	(TIMS). The analysis was run in dynamic mode by switching between masses 308 and
331	309. Each analysis corresponded to 10 blocks of 10 ratios. Samples were always run
332	twice. Total B blank was less than 10 ng corresponding to a maximum contribution of
333	0.2%, which was negligible. Seawater (IAEA-B1) was purified regularly in the same

334	way, in order to check for a possible chemical fractionation due to an uncompleted
335	recovery of B, and to evaluate the accuracy and reproducibility of the overall procedure.
336	Reproducibility was obtained by repeated measurements of the NBS951 and the
337	accuracy was controlled with the analysis of the IAEA-B1 seawater standard ($\delta^{11}B =$
338	38.6 \pm 1.7‰). The ¹¹ B/ ¹⁰ B ratio of replicate analyses of the NBS951 boric acid standard
339	(after oxygen correction) was 4.05045 \pm 0.00130 (2 σ , n=183). The reproducibility of the
340	$\delta^{11}B$ was $\pm 0.32\%$ (2 σ). The mean value obtained on $\delta^{11}B$ of seawater was
341	39.21±0.31‰ (2 σ ; n=20). In order to analyse the δ^{13} C of inorganic carbon, water
342	samples were acidified with ortho-phosphoric acid and shaken for at least two hours to
343	convert all bicarbonate into CO_2 and to reach equilibrium between the dissolved and
344	gaseous phases. Gas samples were then diluted with helium to facilitate the analysis.
345	δ^{13} C was measured on a Gas Chromatograph-Combustion-Isotopic Ratio Mass
346	Spectrometer (GC-C-IRMS). All isotope notations are expressed as δ per mil relative to
347	their respective international standards: Vienna Standard Mean Ocean Water (V-
348	SMOW), atmospheric N_2 (AIR), Vienna Canyon Diablo Troilite (V-CDT), NBS951 and
349	Vienna Pee Dee Belemnite (V-PDB) standards. Reproducibility is $\pm 1.5\%$ for $\delta^2 H$,
350	$\pm 0.2\%$ for $\delta^{18}O_{H2O},\pm 0.3\%$ for $\delta^{15}N,\pm 0.2\%$ for $\delta^{34}S,\pm 0.5\%$ for both $\delta^{18}O_{NO3}$ and
351	$\delta^{18}O_{SO4},\pm0.3\%$ for $\delta^{11}B,$ and $\pm0.3\%$ for $\delta^{13}C_{HCO3}.$
352	For isotope analyses, samples were prepared at the laboratory of the Mineralogia
353	Aplicada i Geoquimica de Fluids research group of the Universitat de Barcelona and the
354	analyses were performed at the Centres Científics i Tecnològics of the Universitat de
355	Barcelona (CCiT-UB), except those of δ^{11} B that were analysed at the BRGM (France)
356	and those of $\delta^{13}C$ that were analysed at the Environmental Isotope Laboratory (EIL) of
357	the University of Waterloo (Canada).
358	4. Results and discussion

359	Groundwater hydraulic head, hydrochemical and isotope data of the two campaigns
360	are reported in Tables 1, 2 and 3.
361	
362	
363	
364	Table 1. Hydrogeological formation, X and Y UTM coordinates, depth (m), hydraulic
365	head (m.a.s.l.), and physico-chemical parameters measured in situ for the sampled
366	points of each field campaign. See Fig. 1 for sampling locations in the Baix Ter basin.
367	R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig.
368	1). (<i>n.d.</i> : Not determined).

ample	Field campaign	Hydrogeological formation	X (UTM)	Y (UTM)	Depth (m)	Hydraulic head (m.a.s.l.)	T (°C)	EC (25 °C) (μS/cm)	pН	Eh (m\
Q ₁	1	Q _D	504970	4654520	28	13.1	14.0	787	7.9	89
Q ₂	1	Qp	508910	4653880	46	-1.4	14.4	596	8.0	46
Q ₃	1	Q _D	508790	4648620	72	16.9	16.7	955	7.7	39
Q ₂	2	Qp	508910	4653880	46	-3.0	18.3	812	7.8	18
Q3	2	Q _D	508790	4648620	72	15.6	18.2	1225	7.7	39
Q4	1	Qs	506280	4653300	7	10.8	15.0	1594	7.4	27
Q5	1	Qs	502300	4649320	10	27.4	16.0	1640	7.6	37
Q_6	1	Qs	503340	4649390	10	22.4	14.6	899	7.6	33
Q ₇	1	Qs	501670	4655680	21	13.4	17.0	843	7.7	36
Q ₈	1	Qs	504920	4656490	20	10.9	16.9	862	7.9	36
Q ₉	1	Qs	505460	4652860	10	12.6	14.0	772	7.9	26
Q ₁₀	1	Qs	504340	4644620	8	60.3	16.3	1180	7.7	42
Q ₁₁	1	Qs	507820	4647100	6	32.0	13.3	722	8.2	36
Q ₁₂	1	Qs	501970	4655900	20	12.3	16.1	773	7.9	34
Q ₁₃	1	Qs	504290	4652570	16	13.1	14.9	836	7.8	44
Q ₁₄	1	Qs	504920	4646740	6	37.7	13.2	886	8.2	37
Q ₁₅	1	Qs	509180	4650980	6	5.2	15.3	2523	7.6	40
Q ₁₆	1	Qs	510970	4644350	6	36.4	14.7	1004	7.8	39
Q ₅	2	Qs	502300	4649320	10	24.8	16.8	2359	7.6	38
Q ₆	2	Qs	503340	4649390	10	n.d.	17.3	1125	7.8	31
Q7	2	Qs	501670	4655680	21	10.2	17.1	1164	7.5	41
Q ₈	2	Qs	504920	4656490	20	10.7	17.7	1383	7.8	33
Q9	2	Qs	505460	4652860	10	n.d.	16.2	1070	7.7	39
Q ₁₀	2	Qs	504340	4644620	8	60.4	16.2	1320	7.4	42
Q ₁₃	2	Qs	504290	4652570	16	8.7	16.2	1219	7.4	39
Q ₁₄	2	Qs	504920	4646740	12	36.1	17.6	949	7.5	36
Q ₁₅	2	Qs	509180	4650980	6	3.8	17.3	2993	8.0	38
Q ₁₆	2	Qs	510970	4644350	6	35.7	22.9	1007	7.8	44
Q ₁₆ Q ₁₇	2	Qs	501720	4647990	n.d.	29.5	17.6	809	7.9	38
	2	Qs	510230	4648070	6	14.2	17.9	875	7.5	40
Q ₁₈	2	Qs	508410	4648070	12	32.8	16.4	999	7.6	40 34
Q ₁₉										
Q ₂₀	2	Qs Qs	503580	4647920	17 17	19.0	15.8	661	7.8 7.5	72
Q ₂₁	2	spring	505090 507650	4650800 4645200	0	15.0 55.0	16.2 15.0	980 629	7.5	44
s	2	spring	507650	4645200	0	55.0	15.4	748	7.9	33
T ₁	1	Tp	508930	4648350	90	21.6	19.5	552	8.0	34
T_2	1	Тр	508830	4651340	100	7.2	14.9	908	8.0	36
T3	1	Tp	503340	4651590	100	27.7	17.5	1176	7.8	37
					110	27.4	16.6	725	8.1	n.c
T ₄	1		505912	4646025		27.4		1005	7.0	34
T ₄ T ₅		Tp			125		16.5	1325	7.8	
T_5	1	T⊳ T⊳	504420	4647820		27.1	16.5	1325 736	7.8 7.8	36
Τ ₅ Τ ₆		T⊳ T⊳ T⊳	504420 511510		125 110 90			736	7.8	
T ₅ T ₆ T ₁	1 1 2	Τ _D Τ _D Τ _D Τ _D	504420 511510 508930	4647820 4646260 4648350	110 90	27.1 -4.5 21.6	16.5 18.5 20.0	736 935	7.8 7.7	36
T ₅ T ₆ T ₁ T ₂	1 1 2 2	T _D T _D T _D T _D	504420 511510 508930 508830	4647820 4646260 4648350 4651340	110 90 100	27.1 -4.5 21.6 11.4	16.5 18.5 20.0 19.8	736 935 1095	7.8 7.7 7.7	36 42
T ₅ T ₆ T ₁ T ₂ T ₃	1 1 2 2 2 2	To To To To To To	504420 511510 508930 508830 503340	4647820 4646260 4648350 4651340 4651590	110 90	27.1 -4.5 21.6	16.5 18.5 20.0	736 935	7.8 7.7	36 42 37
T_5 T_6 T_1 T_2 T_3 T_5	1 1 2 2 2 2 2	To To To To To To To To	504420 511510 508930 508830 503340 504420	4647820 4646260 4648350 4651340 4651590 4647820	110 90 100 100 125	27.1 -4.5 21.6 11.4 22.1 24.4	16.5 18.5 20.0 19.8 17.2 19.1	736 935 1095 1500 1330	7.8 7.7 7.7 7.7 7.9	36 42 37 30
T_5 T_6 T_1 T_2 T_3 T_5 T_6	1 1 2 2 2 2 2 2 2	Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D	504420 511510 508930 508830 503340 504420 511510	4647820 4646260 4648350 4651340 4651590 4647820 4646260	110 90 100 100 125 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5	16.5 18.5 20.0 19.8 17.2 19.1 19.0	736 935 1095 1500 1330 600	7.8 7.7 7.7 7.7 7.9 8.2	36 42 37 30 32
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2	То То То То То То То То То То	504420 511510 508930 508830 503340 504420 511510 499910	4647820 4646260 4648350 4651340 4651590 4647820 4646260 4647360	110 90 100 100 125 110 70	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2	736 935 1095 1500 1330 600 1164	7.8 7.7 7.7 7.7 7.9 8.2 7.7	36 42 37 30 32 42
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ \hline T_6 \\ \hline T_7 \\ T_8 \\ \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2	Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D	504420 511510 508930 508830 503340 504420 511510 499910 501790	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647360 4647360 4643590	110 90 100 125 110 70 156	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1	736 935 1095 1500 1330 600 1164 1374	7.8 7.7 7.7 7.9 8.2 7.7 8.0	36 42 37 30 32 42 35
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το Το Το Το Το Το Το Το Το Το Το Το Τ	504420 511510 508930 508830 503340 504420 511510 499910 501790 507880	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4646260 4647360 4643590 4644460	110 90 100 125 110 70 156 85	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 <i>n.d.</i> 53.9	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4	736 935 1095 1500 1330 600 1164 1374 971	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9	36 42 37 30 32 42 35 15
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 511510 508930 508830 503340 504420 511510 499910 501790 507880 510025	4647820 4647820 4648350 4651340 4651590 4647820 4647820 4647820 4647360 4643590 46445900	110 90 100 125 110 70 156 85 125	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7	736 935 1095 1500 1330 600 1164 1374 971 1053	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9	36 42 37 30 32 42 35 15 18
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ \hline T_6 \\ \hline T_7 \\ T_8 \\ \hline T_9 \\ \hline T_{10} \\ \hline T_{11} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 511510 508930 508830 503340 504420 511510 499910 501790 507880 510025 501590	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647800 4643590 46445900 4644810	110 90 100 125 110 70 156 85 125 130	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4	736 935 1095 1500 1330 600 1164 1374 971 1053 824	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 8.0	36 42 37 30 32 42 35 15 18 91
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 508930 508930 508830 503340 504420 511510 499910 501790 507880 510025 501590 498230	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4646260 46447360 46443590 4644460 4643590 4644460 4649000 4647810 4653260	110 90 100 125 110 70 156 85 125 130 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 nd. 53.9 nd. 23.8 nd.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8	36 42 37 30 32 42 35 15 18 91 45
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To	504420 511510 508930 508830 503340 504420 511510 49910 501790 507880 510025 501590 498230 512180	4647820 4648260 4648350 4651340 4651590 4647820 4647820 4647360 4647360 4644590 46446400 4647810 4653260 4645340	110 90 100 125 110 70 156 85 125 130 110 175	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 nd. 53.9 nd. 23.8 nd. nd. nd.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6	36 42 37 30 32 42 35 15 18 91 45 39
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To	504420 504420 511510 508930 508830 508830 50420 511510 511510 501790 501790 501790 51025 501590 498230 512180 508150	4647820 4646260 4648350 4651340 4651340 4647820 4647820 4647860 4643590 4643590 4644460 4649000 4647810 4653260 4645340	110 90 100 125 110 70 156 85 125 130 110 175 60	27.1 4.5 21.6 11.4 22.1 24.4 -4.5 42.0 nd. 53.9 nd. 23.8 nd. 23.8 nd. 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 8.0 7.8 7.6 7.6 7.6	36 42 37 30 32 42 35 15 18 91 45 39 15
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To	504420 504420 508930 508830 50340 504420 511510 499910 501790 507880 510025 501590 498230 512180 508150 501970	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647360 4647360 4647810 4647810 46453260 46453260 46453420	110 90 100 125 110 70 156 85 125 130 110 175 60 80	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 4.2.0 n.d. 53.9 n.d. 23.8 n.d. n.d. n.d. n.d. 19.3 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1	736 935 1095 1500 11330 600 1164 1374 971 1053 824 994 1137 1449 1389	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.8	36 42 37 30 32 42 35 15 18 91 45 39 15 33
$\begin{array}{c} T_5 \\ T_6 \\ T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \\ T_{16} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To	504420 504420 511510 508930 508830 503340 504420 511510 499910 501790 501790 501790 510225 501590 498230 512180 501970 501970 501930	4647820 4646260 4648350 4651590 4647820 4647820 4647820 4644780 4644780 46447810 4653260 4645340 4645340 465320 4653420 465350 465350 465350 465350 465350 4655500 46555000 46555000 46555000 465550000000000	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22	27.1 4.5 21.6 11.4 22.1 24.4 4.5 42.0 nd. 53.9 nd. 23.8 nd. 23.8 nd. 19.3 nd. 19.3 nd. 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1499 1389 1006	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.6 7.8 7.9	36 42 37 30 32 42 35 15 18 91 45 39 15 33 33 36
$\begin{array}{r} T_5 \\ T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ \hline T_{16} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 508930 508930 508330 503340 504420 511510 499910 501790 501790 501790 501790 501790 501590 498230 512180 508150 501970 501930	4647820 4646260 4648350 4651340 4655340 4647820 4647820 4644260 464780 46443590 4644460 4649300 4645340 4653420 465340 465340 465320 465340 465360 465340 465360 465350 465550 465550 465550 465550 465550 4655500 4655500 4655500 4655500 4655500 4655500 4655500 4655500 4655500 46555000 46555000 46555000 465550000000000	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22	27.1 4.5 21.6 11.4 22.1 24.4 4.5 42.0 nd. 53.9 nd. 23.8 nd. 19.3 nd. 19.3 nd. 19.3 6.5 -5.8	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8	736 935 1095 1500 1330 600 1164 971 1374 971 1053 824 994 1137 1449 938 94 1137 1449 1389 1006 1219	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.6 7.8 7.9 7.5	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40
$\begin{array}{c} T_5 \\ T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{17} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508930 508830 503340 504420 511510 49910 501790 507880 51025 501790 507880 51025 511580 498230 512180 512180 512180 510930 510930 510930	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647820 4647800 46447810 4643260 4647810 4645260 46453420 4645500 4652480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 40	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 nd. 23.8 nd. 23.8 nd. 23.8 nd. 19.3 nd. -6.5 -5.8 23.7	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8 19.2	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 994 1143 994 11449 1389 1006 2414	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.8 7.9 7.5 7.5 7.6	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40 32
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{17} \\ T_{18} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508830 503340 504420 511510 499910 501790 501790 501790 51025 501590 498230 512180 501970 501970 501970 501930 510930	4647820 4646260 4643350 4651540 4651540 4647820 4647820 4643590 4644560 4643590 4644540 46453260 4645340 4645340 4645340 4653450 4653450 4653480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 40 34	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. -6.5 -5.8 23.7 126.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8 19.2 18.0	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 994 1137 1389 1389 1389 1389 2414 837	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.6 7.8 7.9 7.5 7.6 8.0	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40 32 35
$\begin{array}{c} T_5 \\ T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{17} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508930 508830 503340 504420 511510 49910 501790 507880 51025 501790 507880 51025 511580 498230 512180 512180 512180 510930 510930 510930	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647820 4647800 46447810 4643260 4647810 4645260 46453420 4645500 4652480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 40	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 nd. 23.8 nd. 23.8 nd. 23.8 nd. 19.3 nd. -6.5 -5.8 23.7	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8 19.2	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 994 1143 994 11449 1389 1006 2414	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.8 7.9 7.5 7.5 7.6	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40 32 35
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{17} \\ T_{18} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508830 503340 504420 511510 499910 501790 501790 501790 51025 501590 498230 512180 501970 501970 501970 501930 510930	4647820 4646260 4643350 4651540 4651540 4647820 4647820 4643590 4644560 4643590 4644540 46453260 4645340 4645340 4645340 4653450 4653450 4653480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 40 34 10 9	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 <u>n.d.</u> -6.5 -5.8 23.7 126.0 106.3 9.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8 19.2 18.0	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 994 1137 1389 1389 1389 1389 2414 837	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 8.0 8.0 8.0 7.7	36 42 37 30 32 42 35 15 18 91 45 39 15 39 15 33 36 40 32 35 35
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_9 \\ \hline T_{10} \\ \hline T_{11} \\ \hline T_{12} \\ \hline T_{13} \\ \hline T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ \hline T_{17} \\ \hline T_{18} \\ \hline T_{19} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 511510 508830 503340 504420 511510 501790 501790 501790 501790 510025 501590 498230 512180 501570 501970 510930 501930 501930 501930 502550 499460 500770	4647820 4646260 4648350 4651590 4647820 4647820 4647820 4647820 4643590 46447800 4643280 46453260 4645340 4653260 46547500 4653420 46547500 4652480 4652480 4652480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 80 22 22 22 40 34 10	27.1 4.5 21.6 11.4 22.1 24.4 4.5 42.0 nd. 53.9 nd. 23.8 nd. 19.3 nd. 19.3 nd. 19.3 nd. 19.3 2.7 25.7 26.0 106.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.1 16.1 16.1 16.1 16.1 17.8	738 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 2414 1219 2414 837 944	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 7.8 7.6 7.6 7.6 7.8 7.9 7.5 7.6 8.0 8.0 8.0	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40 32 35 35 35
$\begin{array}{r} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ \hline T_6 \\ T_7 \\ T_8 \\ T_9 \\ \hline T_{10} \\ \hline T_{11} \\ T_{12} \\ \hline T_{13} \\ \hline T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ \hline T_{17} \\ \hline T_{18} \\ \hline T_{19} \\ \hline T_{20} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508830 508830 503340 504420 511510 501790 507880 501790 507880 501790 507880 501590 498230 512180 508150 510930 511510 510950 511510 50850 50150 500550 5	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647820 4647820 4647800 4647810 4649900 4647810 46453420 4647500 4652480 4652480 4652480	110 90 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 40 34 10 9	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 <u>n.d.</u> -6.5 -5.8 23.7 126.0 106.3 9.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 19.0 21.2 18.1 19.0 21.2 18.4 19.3 17.1 19.4 19.3 17.1 16.1 16.8 19.2 18.0 17.8 17.7	738 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 994 1149 1389 1006 1219 2414 837 1219 2414	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 8.0 8.0 8.0 7.7	36 42 37 30 32 42 35 15 18 91 45 39 15 33 36 40 32 35 35 35 35 38
$\begin{array}{r} T_5 \\ T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ T_{17} \\ T_{18} \\ T_{19} \\ T_{20} \\ T_{21} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 511510 508830 508830 503440 504420 511510 499910 501780 507880 510025 501580 488230 512180 501970 510930 510930 510930 510930 510930 504505	4647820 4646260 4648350 4651340 4651340 4651590 4647820 4647820 4647820 4647820 4647820 4647820 4647820 46447810 4643240 4653420 4653420 4653450 4652480 4652480 4652480	110 90 100 100 125 110 125 110 125 110 125 110 125 125 126 125 130 175 60 80 22 24 0 9 5	22.1 4.5 21.6 11.4 22.1 24.4 4.5 42.0 n.d. 53.9 n.d. 19.3 n.d. 19.3 n.d. -6.5 -5.8 23.7 126.0 106.3 9.0 102.5	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 19.0 21.2 18.1 19.0 21.2 18.1 19.0 21.2 18.1 19.4 19.3 17.1 17.0 19.4 19.3 17.1 17.1 17.1 17.1 17.1 19.1 19.3 17.1 17.2 20.7 19.4 19.5 19.5 19.5 19.5 19.5 19.5 19.5 19.5	736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 944 11389 1449 1389 1006 2414 2414 837 944 1528 649	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6 8.0 7.5 7.6 8.0 8.0 7.7 7.7	366 421 377 300 324 425 355 183 355 333 366 400 322 355 355 355 355 355 355 355 355
$\begin{array}{c} T_5 \\ \hline T_6 \\ \hline T_1 \\ T_2 \\ T_3 \\ T_5 \\ T_6 \\ T_7 \\ T_8 \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ \hline T_{16} \\ T_{19} \\ T_{20} \\ T_{21} \\ T_{22} \end{array}$	1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	To To To To To To To To To To To To To T	504420 504420 511510 508830 508830 50340 504420 511510 499910 501780 577880 51025 501890 498230 512180 501850 501970 510930 502650 49940	4647820 4646260 4648350 4651340 4651590 4647820 4647820 4647820 4647820 4647800 4647810 4643260 4647810 46453420 46453420 46457800 4652480 46552480 46552480 46552480	110 90 100 125 110 70 156 85 125 60 110 175 60 80 80 22 22 40 34 10 9 9 5 <i>n.d.</i>	27.1 4.5 21.6 11.4 22.1 24.4 4.5 42.0 nd. 53.9 nd. 23.8 nd. 19.3 nd. 19.3 nd. 19.3 nd. 19.3 5.8 23.7 126.0 106.3 9.0 102.5 nd.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 19.1 19.0 21.2 18.4 19.3 18.4 20.7 19.4 19.3 19.4 19.3 17.7 19.4 19.3 17.2 19.4 19.3 17.2 19.4 19.3 17.2 19.4 19.5 19.4 19.5 19.4 19.5 19.4 19.5 19.4 19.5 19.5 19.5 19.5 19.5 19.5 19.5 19.5	738 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 2414 1137 1219 2414 1219 2414 1219 2414 1528 649 1055	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.9 7.5 7.6 7.6 7.6 7.6 8.0 7.9 7.5 7.6 8.0 7.7 7.5 7.6	363 364 374 300 324 429 355 155 188 391 400 325 355 355 355 355 355 388 322 377

Sample	са	Field mpaign	Hydrogeological formation	Depth (m)	Hydraulic head (m.a.s.l.)	T (°C)	EC (25 °C) (μS/cm)	pН	Eh (mV)
Q1	2	1	QD	28	13.1	14.0	787	7.9	8
Q ₂	2	1	QD	46	-1.4	14.4	596	8.0	4
Q ₃	<u> </u>	1	QD	72	16.9	16.7	955	7.7	39
Q_2	÷.,	2	QD	46	-3.0	18.3	812	7.8	18
Q_3	۳.	2	QD	72	15.6	18.2	1225	7.7	39
Q4		1	Qs	7	10.8	15.0	1594	7.4	27
Q5	۳.,	1	Qs	10	27.4	16.0	1640	7.6	37
Q_6	۳.,	1	Qs	10	22.4	14.6	899	7.6	33
Q7	۳.,	1	Qs	21	13.4	17.0	843	7.7	36
Q ₈	۳.,	1	Qs	20	10.9	16.9	862	7.9	36
Q9	۳.	1	Qs	10	12.6	14.0	772	7.9	20
Q ₁₀	۳.	1	Qs	8	60.3	16.3	1180	7.7	4:
	•	1		6	32.0	13.3	722	8.2	30
Q ₁₁	•		Qs						
Q ₁₂		1	Qs	20	12.3	16.1	773	7.9	34
Q ₁₃		1	Qs	16	13.1	14.9	836	7.8	44
Q ₁₄	2	1	Qs	6	37.7	13.2	886	8.2	37
Q ₁₅	٠.	1	Qs	6	5.2	15.3	2523	7.6	40
Q ₁₆	× .	1	Qs	6	36.4	14.7	1004	7.8	39
Q ₅	*	2	Qs	10	24.8	16.8	2359	7.6	38
Q ₆	•	2	Qs	10	n.d.	17.3	1125	7.8	3
Q7	۳.	2	Qs	21	10.2	17.1	1164	7.5	4
Q ₈	۳.	2	Qs	20	10.2	17.1	1383	7.8	33
	•	2		10		16.2	1363	7.8	3
Q ₉	•		Qs		n.d.				-
Q ₁₀	•	2	Qs	8	60.4	16.2	1320	7.4	43
Q ₁₃		2	Qs	16	8.7	16.2	1219	7.4	3
Q ₁₄	2	2	Qs	12	36.1	17.6	949	7.5	30
Q ₁₅	٢.	2	Qs	6	3.8	17.3	2993	8.0	38
Q ₁₆	× .	2	Qs	6	35.7	22.9	1007	7.8	44
Q ₁₇		2	Qs	n.d.	29.5	17.6	809	7.9	38
Q ₁₈	•	2	Qs	6	14.2	17.9	875	7.7	4(
Q ₁₉	•	2	Qs	12	32.8	16.4	999	7.6	34
Q ₂₀	•	2	Qs	12	19.0	15.8	661	7.8	73
	•	2	Qs				980		
Q ₂₁		2		17	15.0 55.0	16.2 15.0	629	7.5	3
s	*	2	spring spring	0	55.0	15.0	748	7.9	3
T ₁		1	T _D	90	21.6	19.5	552	8.0	3
	r -	1	TD	100	7.2	14.9	908	8.0	3
т.					27.7	17.5	1176	7.8	3
T2 T			т.				1170	1.0	
T_3		1	T _D	100					
T₃ T₄		1	TD	110	27.4	16.6	725	8.1	
T₃ T₄ T₅		1 1	T⊳ T⊳	110 125	27.1	16.5	1325	7.8	3-
T ₃ T₄ T₅ T ₆		1 1 1	T⊳ T⊳ T⊳	110					34
T ₃ T ₄ T ₅ T ₆ T ₁		1 1 1 2	T₀ T₀ T₀ T₀	110 125 110 90	27.1	16.5 18.5 20.0	1325	7.8 7.8 7.7	3- 3
T ₃ T₄ T₅ T ₆		1 1 1	T⊳ T⊳ T⊳	110 125 110	27.1 -4.5	16.5 18.5	1325 736	7.8 7.8	3- 31 31
T ₃ T ₄ T ₅ T ₆ T ₁		1 1 1 2	T₀ T₀ T₀ T₀	110 125 110 90	27.1 -4.5 21.6	16.5 18.5 20.0	1325 736 935	7.8 7.8 7.7	3 3 3 3
T_3 T_4 T_5 T_6 T_1 T_2 T_3		1 1 2 2	T₀ T₀ T₀ T₀ T₀ T₀	110 125 110 90 100	27.1 -4.5 21.6 11.4	16.5 18.5 20.0 19.8	1325 736 935 1095	7.8 7.8 7.7 7.7	3. 31 31 42 3
T_3 T_4 T_5 T_6 T_1 T_2 T_3 T_5		1 1 2 2 2 2 2	Τ _Ρ Τ _Ρ Τ _Ρ Τ _Ρ Τ _Ρ Τ _Ρ Τ _Ρ	110 125 110 90 100 100 125	27.1 -4.5 21.6 11.4 22.1 24.4	16.5 18.5 20.0 19.8 17.2 19.1	1325 736 935 1095 1500 1330	7.8 7.8 7.7 7.7 7.7 7.9	3. 31 31 42 31 31
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ \hline T_{6} \\ \end{array}$		1 1 2 2 2 2 2 2 2	T₀ T₀ T₀ T₀ T₀ T₀ T₀ T₀ T₀ T₀	110 125 110 90 100 100	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5	16.5 18.5 20.0 19.8 17.2	1325 736 935 1095 1500	7.8 7.8 7.7 7.7 7.7 7.9 8.2	3- 3- 4: 3- 3- 3- 3:
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ \end{array} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2	T _D T _D T _D T _D T _D T _D T _D T _D	110 125 110 90 100 100 125 110 70	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2	1325 736 935 1095 1500 1330 600 1164	7.8 7.8 7.7 7.7 7.7 7.7 7.9 8.2 7.7	3. 31 42 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	T _D T _D T _D T _D T _D T _D T _D T _D	110 125 110 90 100 100 125 110 70 156	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1	1325 736 935 1095 1500 1330 600 1164 1374	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0	3. 31 4. 31 31 31 31 31 31 31 31 31 31 31 31 31
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο	110 125 110 90 100 100 125 110 70 156 85	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4	1325 736 935 1095 1500 1330 600 1164 1374 971	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9	3. 31 4: 33 34 34 33 4. 34 34 34
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D Τ _D	110 125 110 90 100 100 125 110 70 156 85 125	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7	1325 736 935 1095 1500 1330 600 1164 1374 971 1053	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 7.9	3. 31 4: 32 33 33 34 34 34 34 34 34 34 34 34 34 34
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο	110 125 110 90 100 125 110 70 156 85 125 130	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 8.0 7.9 8.0	3. 3. 4: 3. 3. 3. 3. 4. 3. 3. 1. 1. 1. 1. 9
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το Το Το Το Το Το Το Το Το Το Το Το Τ	110 125 110 90 100 125 110 70 156 85 125 130 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994	7.8 7.8 7.7 7.7 7.7 8.2 7.7 8.0 7.9 7.9 8.0 7.9 8.0 7.8	3. 3. 4. 3. 3. 3. 3. 3. 3. 3. 3. 1. 1. 1. 9. 4.
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το Το Το Το Το Το Το Το Το Το Το Το Τ	110 125 110 90 100 125 110 70 156 85 125 130 130 110 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6	3- 3- 3- 3- 3- 3- 3- 1- 1- 1- 1- 1- 4- 3- 3- 3- 3- 1- 1- 1- 1- 1- 3- 3- 3- 3- 3- 1- 1- 1- 1- 1- 1- 1- 1- 1- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3-
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το Το Το Το Το Το Το Το Το Το Το Το Τ	110 125 110 90 100 125 110 70 156 85 125 130 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994	7.8 7.8 7.7 7.7 7.7 8.2 7.7 8.0 7.9 7.9 8.0 7.9 8.0 7.8	3- 3- 3- 3- 3- 3- 3- 1- 1- 1- 1- 1- 4- 3- 3- 3- 3- 1- 1- 1- 1- 1- 3- 3- 3- 3- 3- 1- 1- 1- 1- 1- 1- 1- 1- 1- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3- 3-
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Τ ₀ Τ ₀ Τ ₀ Τ ₀ Τ ₀ Τ ₀ Τ ₀ Τ ₀	110 125 110 90 100 125 110 70 156 85 125 130 130 110 110	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449	7.8 7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6	3. 3. 4. 3. 3. 3. 3. 4. 3. 1. 9. 4. 3. 9. 4. 3. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1.
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο Τ _ο	110 125 110 90 100 125 110 70 156 85 125 130 110 110 175 60	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 23.8 n.d. 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.4 19.3 17.1 17.0	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137	7.8 7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6	3. 3. 4. 3. 3. 3. 3. 3. 4. 3. 1. 9. 4. 3. 9. 4. 3. 1. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3. 3.
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ \hline T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \\ \hline T_{16} \\ \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το Το Το Το Το Το Το Το Το	110 125 110 900 100 125 110 70 156 85 125 130 110 175 60 80 00 22	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 <u>n.d.</u> 19.3 <u>n.d.</u> -6.5	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 17.0	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389	7.8 7.7 7.7 7.7 7.9 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.8 7.6 7.8 7.9	3 3 4 3 3 3 3 3 3 4 1 1 1 4 3 4 3 1 1 3 3 3 3
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{15} \\ \hline T_{16} \\ \hline T_{16} \\ \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	To To	110 125 110 90 100 125 110 70 156 85 125 130 110 175 60 22 22	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. 19.3 n.d. 19.3 n.d. 5.8	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219	7.8 7.7 7.7 7.7 7.7 7.7 7.9 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.8 7.8 7.6 6 7.6 7.8 7.9 7.5	33 36 42 33 33 33 33 42 42 33 42 44 33 31 44 44 44 44
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \\ T_{16} \\ T_{16} \\ T_{17} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το	110 125 110 90 100 125 110 70 156 85 125 130 110 175 60 80 80 22 22 22 22 22	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. -6.5 -5.8 23.7	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.4 19.4 19.4 19.5 17.1 17.0 19.1 16.1 16.8 19.2	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414	7.8 7.7 7.7 7.7 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.9 8.0 7.9 7.9 7.6 7.6 7.6 7.9 7.5 7.6	33 34 42 33 33 33 34 42 44 33 31 11 11 11 11 11 11 11 11 11 11 11
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{16} \\ T_{17} \\ T_{18} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το	110 125 110 90 100 125 110 70 156 85 125 130 110 175 60 80 80 22 22 22 40 34	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 19.4 19.3 17.1 17.0 19.4 19.3 17.1 17.0 19.4 18.5 18.5 18.5	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837	7.8 7.7 7.7 7.7 8.0 7.9 7.9 8.0 7.9 7.9 7.9 7.8 7.6 7.6 7.8 7.6 7.8 7.6 7.6 7.6 8.0	33 34 42 33 34 33 35 34 44 41 31 31 33 33 34 34 33 33 34 34 33
$\begin{array}{c} {\rm T}_{3} \\ {\rm T}_{4} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{1} \\ {\rm T}_{2} \\ {\rm T}_{3} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{7} \\ {\rm T}_{6} \\ {\rm T}_{7} \\ {\rm T}_{10} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{14} \\ {\rm T}_{15} \\ {\rm T}_{16} \\ {\rm T}_{17} \\ {\rm T}_{18} \\ {\rm T}_{18} \\ {\rm T}_{19} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	To To	110 125 110 90 100 125 110 70 125 130 125 130 110 175 60 80 22 22 22 40 34 40	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d 53.9 n.d 23.8 n.d 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 18.4 19.3 17.1 16.1 16.8 19.2 18.2 18.2 19.1 19.1 18.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.5 19.1 19.4 19.5 19.5 19.4 19.5	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837 944	7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.6 7.8 7.6 7.5 7.6 8.0 7.5 7.5 8.0 7.5	33 36 37 37 37 37 37 37 37 37 37 37 37 37 37
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ \hline T_{6} \\ T_{1} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{8} \\ T_{9} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ \hline T_{16} \\ \hline T_{16} \\ T_{16} \\ T_{17} \\ T_{18} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το	110 125 110 90 100 125 110 70 125 125 130 175 60 80 22 22 22 22 22 40 34 34 99 99	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 19.4 19.3 17.1 17.0 19.4 19.3 17.1 17.0 19.4 18.5 18.5 18.5	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837	7.8 7.7 7.7 7.7 8.0 7.9 7.9 8.0 7.9 7.9 7.9 7.8 7.6 7.6 7.8 7.6 7.8 7.6 7.6 7.6 8.0	33 36 37 37 37 37 37 37 37 37 37 37 37 37 37
$\begin{array}{c} {\rm T}_{3} \\ {\rm T}_{4} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{1} \\ {\rm T}_{2} \\ {\rm T}_{3} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{7} \\ {\rm T}_{6} \\ {\rm T}_{7} \\ {\rm T}_{10} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{14} \\ {\rm T}_{15} \\ {\rm T}_{16} \\ {\rm T}_{17} \\ {\rm T}_{18} \\ {\rm T}_{18} \\ {\rm T}_{19} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το	110 125 110 90 100 125 110 70 125 130 125 130 110 175 60 80 22 22 22 40 34 40	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d 53.9 n.d 23.8 n.d 19.3	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 18.4 19.3 17.1 16.1 16.8 19.2 18.2 18.2 19.1 19.1 18.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.3 17.0 19.4 19.5 19.1 19.4 19.5 19.5 19.4 19.5	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837 944	7.8 7.7 7.7 7.7 7.9 8.2 7.7 8.0 7.9 8.0 7.9 8.0 7.8 7.6 7.6 7.6 7.8 7.6 7.5 7.6 8.0 7.5 7.5 8.0 7.5	34 36 36 37 37 37 37 37 37 37 37 37 37 37 37 37
$\begin{array}{c} {\rm T}_{3} \\ {\rm T}_{4} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{1} \\ {\rm T}_{2} \\ {\rm T}_{3} \\ {\rm T}_{5} \\ {\rm T}_{7} \\ {\rm T}_{8} \\ {\rm T}_{7} \\ {\rm T}_{8} \\ {\rm T}_{7} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{16} \\ {\rm T}_{16} \\ {\rm T}_{17} \\ {\rm T}_{18} \\ {\rm T}_{19} \\ {\rm T}_{20} \\ {\rm T}_{22} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	To Ts Ts Ts Ts Ts Ts Ts Ts	110 125 110 90 100 125 110 70 125 125 130 175 60 80 22 22 22 22 22 40 34 34 99 99	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. 19.3 n.d. 19.3 -6.5 -5.8 23.7 126.0 106.3 9.0	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.1 16.1 16.8 19.2 18.0 17.8 17.7	1325 736 935 1500 1300 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837 944 1528	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 8.0 7.9 7.9 8.0 7.9 7.9 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 7.6 8.0 7.7	34 36 30 30 30 30 30 31 31 31 31 31 31 31 32 31 32 33 33 33 33 33 33 33 33 33 33 33 33
$\begin{array}{c} {\rm T}_{3} \\ {\rm T}_{4} \\ {\rm T}_{5} \\ {\rm T}_{6} \\ {\rm T}_{1} \\ {\rm T}_{2} \\ {\rm T}_{3} \\ {\rm T}_{5} \\ {\rm T}_{7} \\ {\rm T}_{8} \\ {\rm T}_{7} \\ {\rm T}_{8} \\ {\rm T}_{7} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{11} \\ {\rm T}_{12} \\ {\rm T}_{13} \\ {\rm T}_{16} \\ {\rm T}_{16} \\ {\rm T}_{17} \\ {\rm T}_{18} \\ {\rm T}_{19} \\ {\rm T}_{20} \\ {\rm T}_{22} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Το	110 125 100 100 100 125 110 70 156 85 125 130 110 175 60 80 22 22 22 22 22 22 22 22 22 22 22 22 22	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. -6.5 -5.8 23.7 126.0 106.3 9.0 102.5	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 17.0 19.4 19.3 17.1 17.0 19.4 19.3 17.7 19.4 19.3 17.7 19.4 19.3 17.2 19.4 19.5 19.5 19.5 19.5 19.5 19.5 19.5 19.5	1325 736 935 1095 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837 944 4528 649	7.8 7.7 7.7 7.9 8.2 7.7 8.0 7.9 7.9 8.0 7.9 7.9 8.0 7.6 7.6 7.8 7.6 7.8 7.6 8.0 8.0 8.0 8.0 7.7 7.7	33 30 44 43 33 30 42 42 42 42 33 30 44 43 33 30 44 44 33 33 30 30 44 44 33 33 33 30 33 30 33 30 33 33 33 33 33
$\begin{array}{c} T_{3} \\ T_{4} \\ T_{5} \\ T_{6} \\ T_{7} \\ T_{2} \\ T_{3} \\ T_{5} \\ T_{7} \\ T_{8} \\ T_{7} \\ T_{10} \\ T_{11} \\ T_{12} \\ T_{13} \\ T_{14} \\ T_{15} \\ T_{16} \\ T_{17} \\ T_{18} \\ T_{19} \\ T_{17} \\ T_{18} \\ T_{19} \\ T_{20} \\ T_{21} \end{array}$		1 1 2 2 2 2 2 2 2 2 2 2 2 2 2	Το Τς Τς	110 125 110 90 100 125 110 70 125 125 125 125 130 110 175 60 80 22 22 22 40 34 40 34 10 9 5 <i>n.d.</i>	27.1 -4.5 21.6 11.4 22.1 24.4 -4.5 42.0 n.d. 53.9 n.d. 23.8 n.d. 19.3 n.d. -6.5 -5.8 23.7 126.0 106.3 9.0 102.5 n.d.	16.5 18.5 20.0 19.8 17.2 19.1 19.0 21.2 18.1 18.4 20.7 19.4 19.3 17.1 16.3 17.1 16.1 16.8 19.2 18.0 17.8 18.0 17.8 17.7 22.2 17.9	1325 736 935 1500 1330 600 1164 1374 971 1053 824 994 1137 1449 1389 1006 1219 2414 837 944 1528 649 1055	7.8 7.7 7.7 7.9 8.0 7.9 8.0 7.9 7.9 8.0 7.8 7.6 7.8 7.6 7.8 7.6 7.8 7.6 8.0 8.0 7.7 7.7 7.7	n 34 36 36 37 37 37 37 37 37 37 37 37 37

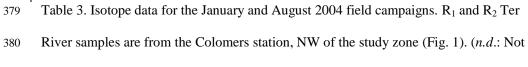
Table 2. Hydrochemical data for the January and August 2004 field campaigns ("*" = DOC concentrations instead of TOC concentrations). R₁ and R₂ Ter River samples are

from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined; *u.d.l.*:

376 under detection limit).

Sample	Field campaign	Hydrogeological formation	HCO 3 ⁻ (mg/L)	SO 4 ²⁻ (mg/L)	Cl ⁻ (mg/L)	NO 3 ⁻ (mg/L)	Na* (mg/L)	K* (mg/L)	Ca ²⁺ (mg/L)	Mg²+ (mg/L)	NH₄* (mg/L)	TOC (mg/L)	Mn (mg/L)	Fe (mg/L)	B (mg/L
Q1 Q2	1 1	Q _D Q _D	413 349	66 48	138 51	u.d.l. u.d.l.	43 44	u.d.l. 3	157 90	23 19	0.15 0.47	1.2 1.0	0.056	0.015	и.a и.a
Q ₂ Q ₃	•	QD	361	117	79	115	37	u.d.l.	181	18	0.15	1.0	0.002	0.010	u.c
Q ₂	2	QD	341	41	61	u.d.l.	45	3	99	19	0.41	0.6	0.335	0.016	и.
Q3	2	QD	335	129	79	144	36	u.d.l.	184	17	0.14	0.9	0.002	u.d.l.	и.
Q4	1	Qs	473	227	269	6	92	4	239	40	0.25	2.3	4.380	0.019	0.1
Q5	1 •	Qs	463	223	200	215	88	u.d.l.	291	28	0.13	2.1	0.002	0.019	и.
Q6 Q7	1 • 1	Qs Qs	388 353	71 111	62 76	88 48	31 30	2 u.d.l.	153 159	18 22	0.15 0.13	1.6 1.0	0.003	0.015	и. и.
Q ₈	• 1	Qs	353	136	99	40	60	3	128	25	0.13	1.4	0.783	0.013	u. u.
Q ₉	• 1	Qs	372	86	84	25	63	4	120	17	0.12	1.4	0.002	0.012	0.2
Q ₁₀	1	Qs	384	114	60	325	41	u.d.l.	245	15	0.18	1.3	0.001	0.014	0.1
Q11	1	Qs	253	60	52	31	31	3	94	13	0.17	3.3	0.003	0.018	и.
Q ₁₂	1	Qs	324	134	81	12	43	2	141	20	0.18	1.1	0.001	0.011	0.0
Q13	1	Qs	401	89	106	51	44	u.d.l.	167	20	0.15	1.9	0.001	0.017	0.0
Q ₁₄	1	Qs	210	77	52	147	29	u.d.l.	128	12	0.15	1.7	0.002	u.d.l.	и.
Q ₁₅	1	Qs	427	277	294	387	94	72	283	76	0.14	3.2	0.001	0.011	0.1
Q ₁₆	2	Qs Qs	351 483	124	76	168	57	u.d.l.	183 331	19 30	0.17	1.9	0.001	u.d.l. u.d.l.	u. u.
Q5 Q6	2	Qs Qs	483 366	321 88	226 59	328 129	123 28	u.d.l. 2	331	30 18	0.14	1.6 0.6	0.001	u.a.ı. u.d.l.	u. u.
Q ₇	2	Qs	399	112	79	129	30	u.d.l.	201	26	0.10	0.5	0.000	0.011	u. u.
Q ₈	2	Qs	337	204	139	51	71	3	174	31	0.08	1.1	0.971	u.d.l.	и.
Q9	2	Qs	358	86	84	26	58	4	130	17	0.11	0.6	0.002	u.d.l.	0.2
Q ₁₀	2	Qs	440	76	50	241	45	u.d.l.	225	13	0.12	0.9	0.002	0.012	0.1
Q ₁₃	2	Qs	405	120	86	66	44	2	178	21	0.08	1.2	0.001	u.d.l.	0.1
Q ₁₄	2	Qs	195	66	55	201	29	u.d.l.	140	13	0.08	0.5	0.002	0.011	и.
Q ₁₅	2	Qs	413	371	362	480	111	68	345	85	0.14	3.4	0.001	u.d.l.	0.1
Q ₁₆	2	Qs	356 301	93 29	55 28	65 60	47 18	u.d.l. u.d.l.	143 116	14 12	0.14	0.6 0.4	0.001	u.d.l. u.d.l.	и. и.
Q ₁₇ Q ₁₈	2	Q _S Q _S	301	29 102	28 47	60 83	18	u.a.i. 6	116	12	0.13	0.4	0.001	u.a.i. u.d.i.	и. и.
Q ₁₈	2	Qs	304	55	52	205	24	u.d.l.	166	14	0.15	0.7	0.001	0.022	u. u.
Q ₂₀	2	Qs	177	52	52	50	29	5	83	11	0.12	0.9	0.001	0.012	0.0
Q ₂₁	2	Qs	313	95	71	45	55	4	124	16	0.21	0.6	0.002	0.011	0.2
S	1	spring	298	64	47	37	29	u.d.l.	110	12	0.18	1.4	0.001	0.011	и.
S T1	2	spring T _D	268 417	58 68	50 43	68 10	31 42	u.d.l. 3	117	13 13	0.15	1.0	0.001	0.013	и. и.
T ₂	1	TD	470	156	87	9	51	3	129	54	0.13	1.3	0.018	0.012	u.
T ₃	1	TD	276	116	123	222	55	u.d.l.	185	22	0.15	1.9	0.001	0.014	и.
T4	1	TD	383	110	60	15	33	49	118	24	0.16	1.2	0.025	0.016	0.0
T ₅	1	TD	430	152	119	222	105	12	178	36	0.20	2.8	0.007	0.012	0.0
T ₆	1	TD	382	59	76	46	57	3	118	20	0.14	1.2	0.007	0.014	и.
T ₁	2	TD	402	55	41	23	35	3	136	12	0.16	0.4	0.001	u.d.l.	и.
T2	2	TD	435	157	74	11	44	3	127	51	0.12	0.7	0.026	u.d.l.	0.0
T3 T	2	TD	376 514	91	180	221 61	68 162	4	214	30 23	0.12	1.7	0.001	u.d.l.	0.0
Τ ₅ Τ ₆	2	T _D T _D	354	118 34	99 70	3	54	11 3	94 100	23	0.18 0.14	0.6 0.3	0.010	u.d.l. u.d.l.	0.1
16 T ₇	2	TD	368	83	66	139	34	u.d.l.	183	14	0.14	0.9	0.007	u.d.l.	u.
T ₈	2	TD	222	107	135	265	58	9	181	24	0.12	1.1	0.007	0.016	и.
T ₉	2	TD	384	31	118	u.d.l.	75	5	81	39	0.16	0.9	0.197	0.013	0.0
T ₁₀	2	TD	533	74	52	u.d.l.	63	2	168	16	0.10	0.4	0.064	0.013	0.0
T ₁₁	2	TD	323	32	46	69	41	3	106	16	0.11	0.8	0.001	0.013	и.
T ₁₂	2	TD	379	52	62	71	33	3	104	45	0.12	0.4	0.002	0.013	и.
T ₁₃	2	TD	392	86	96	46	55	2	146	28	0.12	0.7	0.001	0.010	0.0
T ₁₄	2	T _D	619	87 95	126	u.d.l.	74 114	4	102 110	94 42	0.33	0.5	0.042	0.016	0.0
T ₁₅ T ₁₆	2	T _D T _S	401 388	95 149	130 93	152 63	114 55	3	110	42	0.21	1.2	0.002	0.014	0.
T ₁₆	2	Ts	300	149	102	71	49	u.d.l.	162	37	0.12	0.9	0.002	0.014	u. u.
	2	Ts	372	245	231	419	122	59	223	70	0.23	2.6	0.002	u.d.l.	0.0
T ₁₇	2	Ts	249	30	31	147	15	u.d.l.	121	19	0.14	0.6	0.001	u.d.l.	u
T ₁₇ T ₁₈			348	56	39	89	33	7	137	13	0.14	1.2	0.003	u.d.l.	u
	2	Ts				212	56	6	200	38	0.17	2.2	0.001	u.d.l.	0.
T ₁₈		T _s	350	210	108	212									
T ₁₈ T ₁₉	2			210 30	108 36	6	22	u.d.l.	104	9	0.14	1.0	0.002	0.012	и.
T ₁₈ T ₁₉ T ₂₀ T ₂₁ T ₂₂	2 2 2 2	T _S T _S T _S	350 300 371	30 81	36 49	6 153	22 29	u.d.l.	193	8	0.16	1.1	0.002	0.012	и.
T ₁₈ T ₁₉ T ₂₀ T ₂₁	2 2 2	T _s T _s	350 300	30	36	6	22								u. u. u.





381 determined).

Sample	Field campaign	Hydrogeological formation	δ ¹⁸ 0-H ₂ 0 (‰)	$\delta^2 H$ (‰)	δ ¹⁵ Ν (‰)	δ ¹⁸ O-NO ₃ (‰)	δ ³⁴ S (‰)	δ ¹⁸ O-SO ₄ (‰)	δ ¹³ C-DIC (‰)	δ ¹¹ Β (‰)
Q ₁	1	QD	-5.2	-35.8	n.d.	n.d.	14.7	16.1	-14.9	n.d.
Q ₂	1	QD	-5.5	-37.8	n.d.	n.d.	13.9	13.6	-13.7	n.d.
Q ₃	1	QD	-5.4	-35.4	11.6	8.3	0.4	5.6	-13.6	n.d.
Q ₂	2	QD	-5.9	-37.6	n.d.	n.d.	10.3	12.4	-13.8	n.d.
Q ₃	2	QD	-5.5	-34.9	12.3	8.4	0.9	5.5	-13.7	n.d.
Q4	1	Qs	-5.1	-33.6	32.5	18.1	8.2	13.0	-13.2	34.5
Q5	1	Qs	-5.3	-34.6	15.9	8.9	12.2	10.1	-12.9	n.d.
Q ₆	1	Qs	-5.3	-33.9	11.3	6.8	6.2	6.8	-13.2	n.d.
Q7	1	Qs	-6.0	-40.8	12.2	7.7	6.3	7.8	-11.3	n.d.
Q ₈	1	Qs	-6.5	-44.1	20.5	13.7	9.1	10.1	-12.7	n.d.
Q9	1	Qs	-5.4	-35.3	19.1	10.1	6.8	8.9	-14.0	23.3
Q ₁₀	1	Qs	-5.8	-39.5	10.4	4.4	5.9	4.8	-12.5	25.7
Q ₁₁	1	Qs	-6.3	-39.6	13.6	8.7	5.1	7.8	-16.0	n.d.
Q ₁₂	1	Qs	-6.3	-41.9	13.3	8.1	8.2	8.9	-12.4	26.0
Q ₁₃	1	Qs	-5.3	-35.9	14.7	9.2	6.3	8.2	-13.9	28.3
Q ₁₄	1	Qs	-5.6	-36.8	7.7	5.5	4.0	5.4	-11.3	n.d.
Q ₁₅	1	Qs	-4.8	-31.8	13.5	7.5	2.6	5.8	-14.6	30.4
Q ₁₆	1	Qs	-5.5	-36.9	8.7	4.2	5.3	5.3	-14.0	n.d.
Q ₅	2	Qs	-5.3	-33.5	18.9	5.3	12.7	10.2	-15.5	n.d.
Q_6	2	Qs	-5.3	-33.8	12.3	7.2	6.1	7.0	-13.6	n.d.
Q7	2	Qs	-5.3	-36.3	12.3	6.5	3.0	6.0	-12.0	n.d.
Q ₈	2	Qs	-6.6	-43.9	16.3	9.5	8.0	7.8	-11.8	n.d.
Q ₉	2	Qs	-5.5	-34.8	21.6	10.6	7.7	9.9	-14.1	n.d.
Q ₁₀	2	Qs	-6.0	-40.6	13.4	4.6	6.4	5.1	-16.0	n.d.
Q ₁₃	2	Qs	-5.3	-33.8	15.7	9.1	5.9	8.5	-13.6	n.d.
Q ₁₄	2	Qs	-5.2	-34.8	9.9	4.4	4.6	5.0	-14.7	n.d.
Q ₁₅	2	Qs	-4.9	-31.8	16.2	4.6	3.3	5.3	-14.1	n.d.
Q ₁₆	2	Qs	-5.8	-37.3	7.2	4.3	4.7	6.1	-14.1	n.d.
Q ₁₇	2	Qs	-5.4	-35.6	8.4	4.8	7.2	6.6	-15.0	n.d.
Q ₁₈	2	Qs	-5.6	-38.0	8.2	4.5	-1.4	6.3	-12.2	n.d.
Q ₁₉	2	Qs	-5.5	-38.2	10.5	5.5	3.1	4.9	-13.4	n.d.
Q ₂₀	2	Qs	-5.6	-36.2	13.6	7.4	5.6	6.6	-14.9	9.0
Q ₂₁	2	Qs	-5.6	-36.9	16.6	9.9	5.4	7.5	-14.7	1.4
S	1	spring	-5.8	-37.4	8.6	5.0	5.3	7.3	-14.3	n.d.
S	2	spring	-5.9	-37.7	9.6	6.8	5.4	7.2	-13.5	n.d.
T1	1	T _D	-5.6	-37.8	8.9	6.8	1.6	8.2	-10.2	n.d.
T ₂	1	T _D	-5.2	-35.1	16.0	8.0	-13.5	3.8	-9.0	n.d.
T ₃	1	T _D	-5.1	-33.1	7.6	4.7	4.9	6.0	-13.7	n.d.
T_4	1	T _D	-5.5	-36.3	14.9	10.1	4.9	10.1	-13.3	31.7
T ₅	1	TD	-5.3	-34.7	11.1	5.3	4.2	4.8	-12.5	23.9
T ₆	1	TD	-5.6	-35.7	12.8	6.9	2.3	8.0	-12.0	n.d.
T ₁	2	TD	-5.8	-36.4	10.8	6.8	1.5	7.6	-11.2	n.d.
T ₂	2	TD	-5.3	-35.3	22.6	10.9	-13.4	4.2	-9.1	n.d.
T ₃	2	TD	-5.2	-36.1	11.0	7.0	5.5	6.2	-13.9	n.d.
T ₅	2	TD	-5.9	-37.5	13.7	6.5	5.8	7.9	-8.5	n.d.
T ₆	2	T _D	-5.9	-37.1	12.1	9.1	-2.6	11.1	-11.9	n.d.
T7	2	TD	-5.5	-36.3	10.8	5.2	5.2	6.6	-13.4	n.d.
T ₈	2	T _D	-5.6	-35.7	13.8	6.1	5.3	4.6	-15.4	n.d.
T ₉	2	T _D	-6.1	-39.0	n.d.	n.d.	14.2	12.0	-11.5	n.d.
T ₁₀	2	T _D	-5.7	-37.6	n.d.	n.d.	10.0	10.6	-10.2	n.d.
T ₁₁	2	T _D	-5.4	-39.7	11.6	6.6	6.3	6.2	-13.0	n.d.
T ₁₂	2	T _D	-5.2	-37.5	13.8	7.1	-1.8	4.5	-12.1	n.d.
T ₁₃	2	TD	-5.7	-37.6	11.9	5.6	1.7	5.8	-12.5	n.d.
T ₁₄	2	TD	-5.4	-36.4	n.d.	n.d.	-16.0	4.9	-6.5	n.d.
T ₁₅	2	TD	-5.4	-36.6	12.2	5.0	6.2	5.2	-13.1	n.d.
T ₁₆	1	Ts	-5.4	-34.8	10.7	8.5	-4.1	5.8	-11.3	n.d.
T ₁₆	2	Ts	-5.0	-35.1	13.3	9.4	-1.7	5.5	-11.9	n.d.
T ₁₇	2	Ts	-5.1	-34.3	16.1	1.8	5.9	6.3	-14.5	29.5
T ₁₈	2	Ts	-5.0	-33.9	6.3	3.5	4.1	5.0	-13.5	n.d.
T ₁₉	2	Ts	-5.9	-38.1	9.3	6.2	7.3	9.2	-16.2	n.d.
T ₂₀	2	Ts	-5.4	-36.0	12.2	5.1	3.3	5.6	-13.2	25.5
•20	2	Ts	-6.2	-36.8	5.0	6.3	6.9	5.1	-14.9	n.d.
T ₂₁	-				44.5	6.2	6.6	4.9	-15.6	n.d.
	2	Ts	-5.7	-36.2	11.5	0.2	6.6	4.9	-15.0	
T ₂₁		T _S T _S	-5.7 -5.6	-36.2 -38.2	11.5	6.1	9.4	4.9	-13.0	n.d.
T ₂₁ T ₂₂	2									

4.1. Hydrodynamic data and potentiometric map

385 Hydraulic head measurements in the Quaternary aquifer conducted during the August

campaign were used to draw the potentiometric contour lines shown in Fig.1, as this

387	represents the largest pressure in the groundwater system resources. The generated
388	potentiometric map shows that groundwater flow lines were mainly oriented along a
389	south to north trend (from the Gavarres massif to the Ter River) (Fig. 1) although close
390	to the Ter River, groundwater flow changed to a west-to-east direction towards the sea.
391	This is in agreement with the conceptual flow model described in previous studies (e.g.,
392	Vilanova and Mas-Pla, 2004). The potentiometric map also reflects the depression cone
393	of the Gualta village resulting from the intense groundwater withdrawal activity of its
394	supply wells. However, it was not possible to draw a consistent potentiometric plot of
395	the Tertiary aquifer that was able to corroborate the upward vertical flow line
396	connecting the underlying confined fractured Tertiary unit to the shallow Quaternary
397	aquifer that was suggested by Vilanova and Mas-Pla (2004 et al. (2008). Potentiometric
398	levels in the Tertiary aquifer may vary seasonally due to groundwater pumping,
399	controlling the recharge relation with the Ter River alluvial aquifer.
400	4.2. δ^2 H and δ^{18} O data. Sources of recharge
401	Fig. 2 shows that δ^{2} H and δ^{18} O of groundwater samples from both campaigns
402	mostly plot ted under against the the annual local Local Mmeteoric Wwater Lline

403 (LMWL, (Vilanova, et al., 200<u>8</u>4). Samples mostly plot under the LMWL.

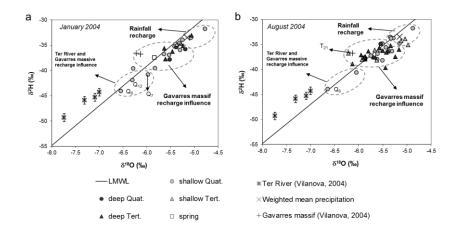




Figure 2. $\delta^{18}O_{H2O}$ and $\delta^{2}H$ of the Baix Ter groundwater samples collected in January 2004 (a) and August 2004 (b). The annual_-Local Meteoric Water Line (LMWL) follows the equation $\delta^{2}H = 7.98(\pm 2.71) \delta^{18}O + 7.85(\pm 0.47)$ (r²=0.924, n=23) (Vilanova et al., 200<u>8</u>4), whose slope is equal to that of the neighbouring areas ($\delta^{2}H = 7.9 \delta^{18}O +$ 9.8; Neal et al., 1992).

However, the wide range of $\delta^2 H$ and $\delta^{18} O$ values from the Quaternary aquifer 410 indicates the implication of several recharge flow systems affecting the aquifer, with 411 distinct hydrogeological characteristics, affecting the aquifer. Some of the samples fall 412 very close to the weighted mean precipitation ($\delta^2 H = -33.5\%$, $\delta^{18} O = -5.2\%$) calculated 413 414 from the Mas Badia station data (located in the Baix Ter basin; Fig. 2) showing the influence of the infiltration of rainfall into the basin. 415 Three <u>S</u>-samples located at the NW of the shallow Quaternary aquifer $(Q_7, Q_8 and$ 416 Q₁₂) yielded lighter isotope compositions with values similar to those of the Ter River 417 reported by Vilanova (2004; δ^2 H from -50 to -45‰, δ^{18} O from -8 to -7‰), indicating a 418 contribution from the Ter River to the alluvial aquifer groundwater. These $\delta^2 H$ and 419 δ^{18} O from the Ter River waters are the lightest observed in the area, explained by the 420 421 fact that the Ter River discharge originates at a higher recharge altitude in the Pyrenees

422	Mountains. Thus, the isotope compositions of the water molecule identify a contribution
423	from the Ter River to the alluvial aquifer groundwater in the NW part of the study zone.
424	Finally, some other samples from the Quaternary aquifer present $\delta^2 H$ and $\delta^{18} O$
425	compositions intermediate between those influenced by the rainfall and those influenced
426	by the Ter river water (Fig. 2) but also close to - H and O Isotope compositions of these
427	samples, however, are very close to those of sample T_{21} , located in the Gavarres massif
428	foothill (south of the study area, Fig. 1). Thus, Fthese samples can be geochemically
429	and isotopically considered as representative of the recharge from the Gavarres massif,
430	given its very low mineralization and its isotope composition (Fig.2). As irrigation
431	demand is fully covered by groundwater in the sampled area, the potential effects of
432	irrigation returns on groundwater isotopic composition would not in any case modify
433	the recharge model herein proposed. that is very similar to the groundwater from the
434	Paleozoic materials in the Gavarres massif (Vilanova, 2004; Fig. 2).
435	In Tertiary aquifers, Mmost of the groundwater samples from the Tertiary aquifers
436	fell between the weighted mean precipitation signature and the isotope composition of
437	groundwater from the Gavarres massif (Fig. 2). They present a narrower range of $\delta^2 H$
438	and $\delta^{18}O$ compositions, although they overlap with the intermediate isotopic
439	composition of the Quaternary aquifer groundwater samples (Fig. 2). This overlap
440	suggests that both aquifers share a common source of recharge or are somehow
441	connected. This is consistent with the conceptual model described by Vilanova and
442	Mas-Plaet al. (20084) in which an upward groundwater flow was proposed connecting
443	the Tertiary aquifer to the deep Quaternary aquifer in the northern part of the area.
444	Therefore, the contribution from the Tertiary units towards the Quaternary aquifer
445	cannot be discarded despite the fact that this could not be supported by the
446	potentiometric map.

4.3. Hydrochemical data

448	Chemical data for groundwater samples collected in the Baix Ter basin (Tables 1
449	and 2) showed a $HCO_3^{-}-Ca^{2+}-Mg^{2+}$ facies, in accordance with the hydrochemistry being
450	controlled by carbonate dissolution reactions that occur throughout the Tertiary
451	materials and alluvial formations. The rapid kinetic of carbonate dissolution hides the
452	hydrochemical characteristics acquired from the igneous and metamorphic rocks of the
453	Gavarres massif (Vilanova et al., 2008). Groundwater pH values were all above 7.4,
454	HCO_3^- concentrations were between 177 and 619 mg $L^{\text{-1}}$ and EC varied from 552 μS
455	cm^{-1} to 2993 µS cm ⁻¹ .
456	In all the studied area, NO ₃ ⁻ concentrations presented a wide range of values in both
457	the Quaternary and Tertiary aquifers, from samples with NO3 ⁻ below the detection limit
458	(0.1 mg L^{-1}) to concentrations up to 480 mg L ⁻¹ . 60% of the studied samples had NO ₃ ⁻¹
459	levels above the legal threshold of 50 mg L^{-1} for drinking water (EC, 1998). No NO_2^{-1}
460	was detected. Ammonium concentration ranged between 0.08 mg L^{-1} and 0.47 mg L^{-1} . It
461	<u>can be observed that The NO₃⁻ concentrations of the river samples presented values of 9</u>
462	and 7 mg L^{-1} , consistent with surface water nitrate values and lower than the monthly
463	NO ₃ ⁻ average for the Ter River (15 mg L ⁻¹ ; σ = 5.1, n = 37) between 2003 and 2006
464	(ACA, 2015). However, nitrate concentration in aquifers showed a diffuse spatial
465	distribution.
466	Nitrate spatial distribution shows a diffuse regional pattern: iIn shallow aquifers (Qs
467	and T_s), nitrate concentrations ranged from 6 to 480 mg L ⁻¹ , while in deeper aquifers
468	they went from values below detection limit up to 265 mg L^{-1} . This distribution does not
469	seem to be linked to any specific groundwater flow direction nor limit of the aquifer
470	units. It can be explained by the highly complex hydrogeology of the study zone and its
471	distinct recharge areas, and by the mixing of waters from distinct origins and qualities

472	within the well borehole. Several factors such as the intended exploitation of different
473	levels to increase the well efficiency, the possible lack of well casing derived from an
474	incomplete borehole construction, and/or the presence of preferential flow paths through
475	fractures or fault zones that connect local and regional flow systems, i.e. Quaternary and
476	Tertiary aquifers could account for the mixing of waters. Moreover, the intensive
477	pumping during irrigation and low rainfall periods can also enhance re-circulation
478	between aquifer levels, mainly from the shallow to deeper ones, resulting in a decrease
479	of the quality of the water resources stored in the deeper aquifer layers. It should then be
480	noticed that nitrate concentrations are more representative of the unknown well
481	characteristics than of the hydrogeological layer where the borehole is drilled.
482	The lowest NO_3^- contents in the Quaternary aquifer were observed near the Ter
483	River suggesting some influence from induced stream recharge; and in the SE area, near
484	the Gavarres Range, in the Tertiary aquifer.
485	During the first sampling campaign, two samples from the shallow Quaternary
486	aquifer (Q ₄ and Q ₈ , Table 2) presented NO ₃ ⁻ concentrations of 6 mg L^{-1} and 13 mg L^{-1} ,
487	respectively, coupled with high levels of Mn (4.4 and 0.8 mg Mn L^{-1}) and around 2 mg
488	L^{-1} of total organic carbon. Two samples in the Q_D (Q_1 and Q_2) and three samples in T_D
489	aquifers (T ₉ , T ₁₀ and T ₁₄) had NO_3^- below detection limit, an Eh value below 200 mV
490	and showed the highest ammonium and manganese concentrations (Tables 1 and 2,
491	Fig.3). Moreover, NO_3^- in Q_2 has been monitored through time and has always been
492	below detection limit. In our study, the ammonium content in Q2 displayed the highest
493	value (0.47 mg L^{-1}) . These characteristics are typical of groundwater under reducing
494	conditions, and would suggest that they are undergoing denitrification processes.
495	However, measured TOC concentrations for Q_1 , Q_2 , T_9 , T_{10} and T_{14} (between 0.4 and

497 oxidation of organic matter in anaerobic conditions (Rivett et al., 2008), but they may

498 indicate the presence of organic matter that could represent a residual content after

499 previous consumption by heterotrophic denitrifying bacteria.

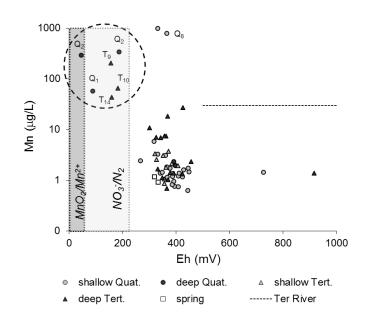
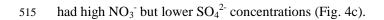




Figure 3. Mn concentrations plotted against the Eh values of the groundwater samples. Eh ranges of MnO_2/Mn^{2+} and $NO_3^-/N_{2(g)}$ redox pairs are taken from Rivett et al. (2008).

505	Some of the samples with high NO_3^- concentration (Q ₅ , Q ₁₀ , Q ₁₅ and Q ₁₆ from Q ₈ ,
506	T_{17} and T_{20} from T_S , and T_3 , T_5 and T_8 from T_D) also presented high sulphate and
507	chloride concentrations (up to 371 and 362 mg L^{-1} , respectively) (Fig. 4a, b).
508	Considering that Cl ⁻ is a conservative element largely unaffected by physical, chemical
509	and microbiological processes occurring in the groundwater (Altman and Parizek,
510	1995), the $[NO_3^-]/[Cl^-]$ ratio can be used to eliminate the potential effect of dilution. In
511	Fig. 4c, sulphate concentration is plotted against the [NO ₃ ⁻]/[Cl ⁻] ratio. Groundwater
512	SO_4^{2-} varied between 29 and 371 mg L ⁻¹ , with an average value of 108 mg L ⁻¹ (n = 64).
513	But a set of samples, with $1 < [NO_3^-]/[Cl^-] < 2$, present moderate $SO_4^{2^-}$ concentrations but



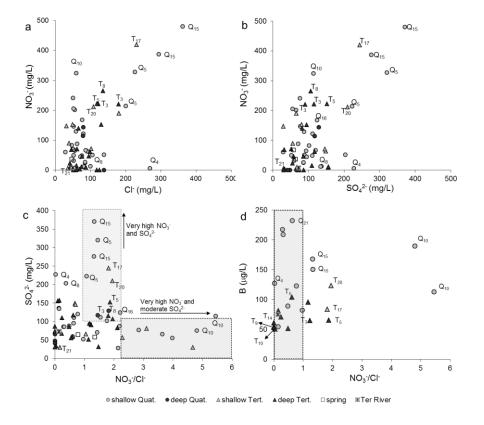
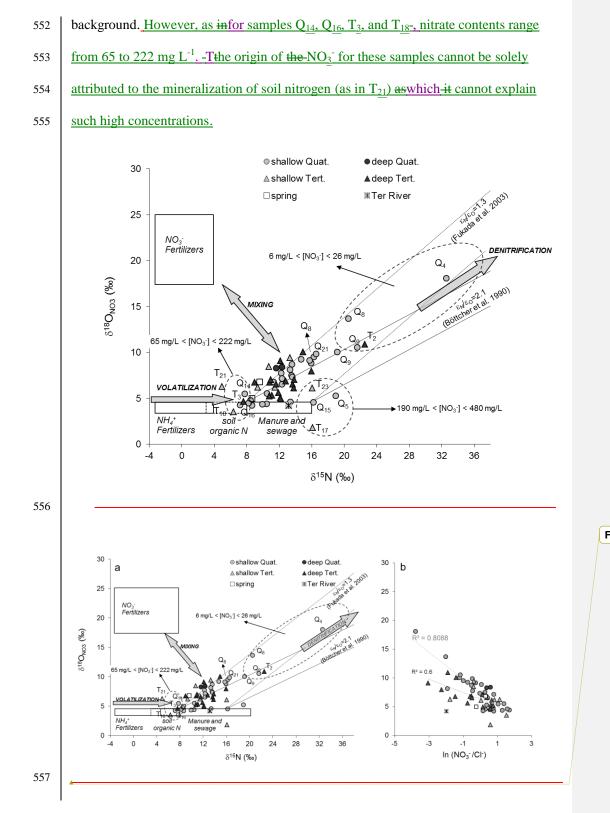


Figure 4. a) NO₃⁻ concentration versus Cl⁻ concentration, b) NO₃⁻ concentration versus SO₄²⁻ concentration, c) SO₄²⁻ concentration versus (NO₃⁻/Cl⁻) ratio, and d) B concentration versus (NO₃⁻/Cl⁻) ratio.

519 520

Since no evaporitic or gypsum outcrops nor disseminated pyrite exist in the study area, these SO_4^{2-} concentrations must originate from anthropogenic sources such as manure, synthetic fertilizers or sewage. High Cl⁻ concentrations can be caused by the input of organic fertilizers since they generally show elevated chloride concentrations (Karr et al., 2001; Menció et al. 2016). All these observations suggest that both the mineral and the organic fertilizers are the major vectors of contamination.

527	In most of samples, B concentration was below the detection limit. However, B
528	concentrations around 0.1-0.2 mg L^{-1} have been measured in samples with high nitrate,
529	sulphate and chloride concentrations (e.g. Q10 and Q15, Fig. 4d) suggesting sewage and
530	manure as other potential contamination sources. However, as seen in Fig. 4d, samples
531	with the highest B concentration (up to 232 μ g/L) presented intermediate nitrate
532	concentrations (25-45 mg $NO_3^{-1}L^{-1}$), showing that the presence of B in groundwater is
533	not necessarily linked to high NO_3^- concentrations.
534	Thus, our results show that groundwater is probably affected by more than one
535	source of contamination and that natural denitrification may be acting in some areas.
536	However, , but an the unambiguous identification of these sources and processes based
537	on the sole hydrochemical data is somewhat difficult as the signal may be hindered by
538	the mixing of groundwaters from different layers and recharge flow systems.
539	4.4. Isotope data. Pollution sources and attenuation processes
559	4.4. Isotope data: I onution sources and attendation processes
540	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻
540	4.4.1. δ^{15} N and δ^{18} O of NO ₃
540 541	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for
540 541 542	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for
540 541 542 543	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3).
 540 541 542 543 544 	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3). As seen in Fig. 5 <u>a</u> , five groundwater samples (Q ₁₄ and Q ₁₆ from Q ₈ , T ₃ from T _D ,
 540 541 542 543 544 545 	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3). As seen in Fig. 5 <u>a</u> , five groundwater samples (Q ₁₄ and Q ₁₆ from Q ₈ , T ₃ from T _D , and T ₁₈ and T ₂₁ from T ₈) presented δ^{15} N values <u>compatible with comparable to those of</u>
 540 541 542 543 544 545 546 	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3). As seen in Fig. 5 <u>a</u> , five groundwater samples (Q ₁₄ and Q ₁₆ from Q ₅ , T ₃ from T _D , and T ₁₈ and T ₂₁ from T ₈) presented δ^{15} N values <u>compatible with comparable to those of</u> soil organic nitrogen (from +3 to +8‰ , Table 4), fertilizers (-4 to +8‰) and sewage (+5
 540 541 542 543 544 545 546 547 	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3). As seen in Fig. 5 <u>a</u> , five groundwater samples (Q ₁₄ and Q ₁₆ from Q ₅ , T ₃ from T _D , and T ₁₈ and T ₂₁ from T ₅) presented δ^{15} N values <u>compatible with comparable to those of</u> soil organic nitrogen (from +3 to +8‰, <u>Table 4</u>), fertilizers (-4 to +8‰) and sewage (+5 <u>to +20‰)</u> ; (<u>Table 4</u>). Within these samples, only sample T ₂₁ presented low nitrate,
 540 541 542 543 544 545 546 547 548 	4.4.1. δ^{15} N and δ^{18} O of NO ₃ ⁻ NO ₃ ⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3). As seen in Fig. 5 <u>a</u> , five groundwater samples (Q ₁₄ and Q ₁₆ from Q ₈ , T ₃ from T _D , and T ₁₈ and T ₂₁ from T ₈) presented δ^{15} N values <u>compatible with comparable to those of</u> soil organic nitrogen (from +3 to +8‰, <u>Table 4</u>), fertilizers (-4 to +8‰) and sewage (+5 to +20‰) ₇ . (<u>Table 4</u>). Within these samples, only sample T ₂₁ presented low nitrate, sulphate and chloride concentration (6 mg L ⁻¹ NO ₃ ⁻ , 36 mg L ⁻¹ Cl ⁻ and 30 mg L ⁻¹ SO ₄ ²⁻).



Formatted: Font: 12 pt

558	Figure 5. <u>a)</u> Variations of the δ^{15} N and δ^{18} O of dissolved NO ₃ ⁻ in groundwater according
559	to their hydrogeological unit. Isotope ranges of the main NO_3^- sources listed in Table 4
560	are also represented. The extreme isotopic fractionation ratios from the literature are
561	$\epsilon_N/\epsilon_O = 2.1$ (Böttcher et al., 1990) and $\epsilon_N/\epsilon_O = 1.3$ (Fukada et al., 2003). b) $\delta^{18}O_{NO3}$
562	values plotted against $ln(NO_3^-/Cl^-)$ according to their hydrogeological unit. R ² values
563	corresponding to the linear regressions for shallow Quat. and deep Tert. Units are also
564	reported.
565	
566	However, as in samples Q_{14} , Q_{16} , T_3 , and T_{18} nitrate contents range from 65 to 222
567	$mg L^{-1}$ the origin of the NO ₃ ⁻ for these samples cannot be solely attributed to the
568	mineralization of soil nitrogen (as in T_{24}) as it cannot explain such high concentrations.
569	Thus, other sources of NO3 ⁻ must be considered though a small contribution of soil
570	organic nitrogen is possible (Wassenaar, 1995). Nitrate derived from ammonium
571	fertilizers present δ^{15} N values between -4 and +4‰ (Table 4). This value can be
572	enriched in ¹⁵ N by volatilization processes leading to values in the range of soil
573	nitrogen, as it was observed by Vitòria (2004) in the Maresme region (Catalonia, NE
574	Spain), where mineral fertilizers were shown to be the only source of NO ₃
575	δ^{15} N value of NO ₃ ⁻ produced after nitrification would be similar to that of the
576	former ammonium affected by volatilization because of the large isotopic fractionation
577	occurring when nitrification is stimulated by e.g. large amounts of available \mathbf{NH}_4^+
578	(Kendall 2007 and references therein). This would explain the lack of nitrite in the area.
579	Therefore, synthetic ammonium fertilizers could be the source of NO_3^- for Q_{14} , Q_{16} , T_3
580	and T ₁₈ samples. Nevertheless, as seen in Fig. 5, nitrate in these samples could also
581	result from a mixing between NO3 ⁻ derived from synthetic fertilizers and NO3 ⁻ derived
582	from manure or sewage (+8 to + 20‰, Table 4). Therefore, although a small

583	contribution of soil organic nitrogen is possible (Wassenaar, 1995), measured isotope
584	values may originate from synthetic fertilizers or sewage/manure sources or from a
585	mixing of both (Fig. 5a).
586	
587	However, the main group of samples presented δ^{15} N ranging between +8 and
588	$\pm 16\%$, indicating that NO ₃ ⁻ may originate from ¹⁵ N enriched anthropogenic organic
589	matter (manure or sewage) (Fig. 5).

- Table 4. Ranges of nitrate, sulphate, boron and dissolved inorganic carbon isotope
- 591 compositions of the main potential sources of nitrate obtained from the literature.

NO ₃ ⁻ source Isotope ratio (‰)	Pig manure	Mineral fertilizers	Sewage	Soil
$\delta^{15}N$	+8 +16	-4 +4	+8 +20	+3 - +8
	Vitòria (2004)	Bateman and Kelly (2007), Kendall et al. (2007), Vitòria et al. (2004)	Aravena and Mayer (2010), Vane et al. (2010), Curt el al. (2004)	Aravena and Mayer (2010), Heaton (1986), Kendall et al. (2007)
$\delta^{18}O_{NO3}$	+3.4 +4.6	+17 - +25	+3.4 +4.6	+3.4 +4.6
	Estimated in this study according to eq.5	Aravena and Mayer (2010), Vitòria et al. (2004), Xue et al. (2009)	Estimated in this study according to eq.5	Estimated in this study according to eq.5
$\delta^{34}S$	-0.9 -+ 5.8	0 +10	+7.6 - +11.7	0 +6
	Cravotta (1997)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)
$\delta^{18}O_{SO4}$	+3.8 - +6	+9 - +15	+9 - +11.1	0 +6
	Otero et al. (2007), Vitòria (2004)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)
$\delta^{11} B$	+19.5 - +42.4	-9 -+ +15	-7.7 - +12.9	-
	Widory et al. (2005)	Komor (1997), Widory et al. (2005), (2013)	Bassett et al. (1995), Vengosh et al. (1994), Widory et al. (2013), Xue et al. (2009)	-
$\delta^{13}C_{HCO3}$	-23.8 16.4	-35 — -24	-2513	-23
	Cravotta (1997), Vitòria (2004)	Vitòria et al. (2004)	Jurado et al. (2013), Li et al. (2010), Waldron et al. (2001)	Clark and Fritz (1997)

NO3 ⁻ source	Pig manure	Mineral fertilizers	Sewage	Soil
Isotope ratio (‰)				
$\delta^{15}N$	+8-+16	-4 +8	+5 +20	+3 +8
	Vitòria (2004)	Vitòria et al. (2004), Michalski et al. (2015)	Aravena and Mayer (2010), Vane et al. (2010), Curt el al. (2004)	Aravena and Mayer (2010), Heaton (1986), Kendall et al. (2007)
$\delta^{18}O_{NO3}$	+3.4 +4.6	+17 - +25	+3.4 +4.6	+3.4 +4.6
	Estimated in this study according to eq.5	Aravena and Mayer (2010), Vitòria et al. (2004), Xue et al. (2009)	Estimated in this study according to eq.5	Estimated in this study according to eq.5
$\delta^{34}S$	-0.9 +5.8	0 +10	+7.6 - +11.7	0 +6
	Cravotta (1997)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)
$\delta^{18}O_{SO4}$	+3.8 - +6	+9+ 15	+9 +11.1	0 +6
	Otero et al. (2007), Vitòria (2004)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)
$\delta^{11}B$	+19.5 - +42.4	-9 -+ +15	-7.7 - +12.9	-
	Widory et al. (2005)	Komor (1997), Widory et al. (2005), (2013)	Bassett et al. (1995), Vengosh et al. (1994), Widory et al. (2013), Xue et al. (2009)	-
$\delta^{13}C_{HCO3}$	-23.8 16.4	-35 — -24	-2513	-23
	Cravotta (1997), Vitòria (2004)	Vitòria et al. (2004)	Jurado et al. (2013), Li et al. (2010), Waldron et al. (2001)	Clark and Fritz (1997)

594	Most of the samples presented δ^{15} N ranging between +8 and +16‰, indicating that
595	NO ₃ may originate from ¹⁵ N-enriched anthropogenic organic matter (manure or
596	<u>sewage) (Fig. 5a).</u> Finally, 8 ¹⁵ N values higher than +16‰ were observed in eleven
597	samples. Four of these samples (Q5 and Q15 from Q8, and T_{17} and T_{23} from T_8) can be
598	explained by volatilization processes as they showed high NO3 ⁻ concentrations (between
599	190 and 480 mg L^{-1}) and $\delta^{18}O_{NO3}$ values up to $+6\%$. By contrast, Finally, some samples
600	(Q ₄ , Q ₈ and Q ₉ , from Q ₅ , and T ₂ from T _D) presented five other samples with $\delta^{15}N$ values
601	also-higher than +16‰, coupled to low NO ₃ ⁻ contents (between 6 and 26 mg L ⁻¹ , Table
602	2) and high $\delta^{18}O_{NO3}$ values (close to +10‰). (Q ₄ , Q ₈ and Q ₉ , from Q ₈ , and T ₂ from T _D)
603	have more likely been affected by denitrification since their NO3 ⁻ contents were low
604	(between 6 and 26 mg L ⁻¹) and their $\delta^{48}\Theta_{NO3}$ were close to +10%.
605	The range of δ^{18} O of NO ₃ ⁻ for NH ₄ ⁺ fertilizers, soil nitrogen and manure and
606	sewage provided in Table 4 and plotted in Fig. $5\underline{a}$ (+3.4‰ to +4.6‰), has been
607	estimated according to eq. 5 (Anderson and Hooper, 1983; Hollocher, 1984; Kendall et
608	al., 2007), where the $\delta^{18}O_{H2O}$ values are the highest and lowest groundwater $\delta^{18}O$
609	measured in the Baix Ter basin, and the $\delta^{18}O_{O2}$ is that of the atmospheric O_2 (+23.5‰;
610	Horibe et al., 1973).
611	$\delta^{18}O_{NO3} = 2/3(\delta^{18}O_{H2O}) + 1/3(\delta^{18}O_{O2}) $ (5)
612	$\delta^{18}O_{NO3}$ values measured in the groundwater samples ranged from +1.8‰ to
613	+18.1% (Fig.5b). While nitrate fertilizers are currently applied onto local crops their
614	direct contribution to groundwater nitrate must be discarded as δ^{18} O and δ^{15} N of
615	groundwater NO_3^- fall very far from nitrate fertilizers values (Fig. 5 <u>a</u>). Moreover, most
616	of samples had $\delta^{18}O_{NO3}$ higher than the calculated values for full equilibrium with the
617	$\delta^{18}O$ of groundwater. Both results could be interpreted as a consequence of three

618	different processes: i) the mineralization-immobilization-turnover (MIT) process, ii) the
619	higher consumption of NO_3^- from mineral fertilizers compared to that of ammonium in
620	the root zone and iii) the reduction of NO_3^- via denitrifying bacteria. The MIT process
621	consists of a microbial-mediated immobilization of nitrate N as organic nitrogen, the
622	subsequent mineralization of this organic nitrogen to ammonium, and finally the
623	nitrification of this ammonium back to NO_3^- (Mengis et al., 2001). This turnover
624	process results in an important ^{18}O depletion of the initial $\delta^{18}\text{O}_{NO3}$ of the synthetic
625	fertilizers (+17‰ to +20‰, Table 4). As synthetic fertilizers are currently used in the
626	area, MIT process must be very active in order to explain why our results do not show
627	the low δ^{15} N and high δ^{18} O values of nitrate from synthetic fertilizers. This indicates all
628	NO ₃ ⁻ from synthetic fertilizers that infiltrated underwent this process and that this
629	source cannot be dismissed.

As pig manure is mainly liquid, the infiltration of ammonium from manure through 630 631 the non-saturated zone to the saturated one is faster than that of nitrate from solid synthetic fertilizers, which need to be dissolved by rain or irrigation. Ammonium soil 632 633 sorption capacity can be considered negligible as the soil is already saturated due to the 634 long-standing fertilization practices affecting the area. Ammonium is also fast and completely nitrified into nitrate in the non-saturated zone. All these elements favour 635 ammonium from pig manure to reach the saturated zone and to be incorporated as 636 nitrate into the polluting groundwater. On the contrary, nitrate from the slow release of 637 638 synthetic fertilizers remains slightly longer on the agricultural soil, increasing the possibility of being absorbed by roots or of being incorporated and stored in the soil 639 organic matter pool (by means of the MIT process). It could then be slowly rereleased 640 641 for either uptake by crops or export into the hydrosphere (Sebilo et al., 2013). Finally, the reduction of NO₃⁻ via denitrifying bacteria, which is characterized by a heavy-642

643	isotope enrichment of both the δ^{15} N and δ^{18} O of the residual nitrate, can overprint the
644	mixing of potential end-members and can significantly alter both the NO3 ⁻ concentration
645	(i.e. attenuation) and corresponding N and O isotope compositions.
646	δ^{15} N and δ^{18} O of NO ₃ from the Ter River samples were in agreement with a
647	wastewater origin.
648	Ten of the samples had $\delta^{18}O_{NO3}$ and $\delta^{15}N$ higher than +8‰ and +15‰, respectively.
649	Fig. 5 <u>a</u> shows that these samples roughly aligned following a ε_N : ε_0 ratio of 2, consistent
650	with natural denitrification (Kendall et al., 2007). This means that the nitrate isotopic
651	compositions but also the low nitrate concentration measured in those samples result
652	from natural denitrification processes occurring in the aquifers. This is confirmed by
653	Fig. 5b, in which a negative linear correlation between $\delta^{18}O_{NO3}$ and $\ln(NO_3/C\Gamma)$ is
654	observed for these samples, indicating that denitrification is taking place (Vitòria et al.
655	<u>2008).</u> The highest denitrified samples (i.e. with the higher coupled $\delta^{18}O_{NO3}$ and $\delta^{15}N$)
656	were observed either in the shallow Quaternary levels near the Ter River (Q_4, Q_8, Q_9) or
657	in the Tertiary aquifers (T_2). Moreover, the NO ₃ ⁻ concentration measured below the
658	detection limit in the samples Q_1 , Q_2 , T_9 , T_{10} and T_{14} (Fig. 2) can also be interpreted as
659	resulting of natural denitrification. Considering that no significant variations were
660	identified in both the isotope and chemical compositions of our samples between both
661	<u>campaigns,</u>
662	During the second sampling campaign, 19 samples from the previous campaign were
663	resampled, and among those only 4 showed a significant decrease in their NO3 ⁻
664	concentration. Among these only two showed corresponding significant shifts in their
665	isotope and chemical compositions, in agreement with natural denitrification (Q_{10} , T_5).
666	This suggests that it can be inferred that natural denitrification had a moderate activity
667	and/or that NO_3^- attenuation was balanced by the input of new NO_3^- into the aquifer.

668 **4.4.2.** δ^{34} S and δ^{18} O of SO₄

 SO_4^{2-} isotope compositions ranged between -16.0 and +14.7% for $\delta^{34}S$, with an 669 average value of +4.5% (n = 64), and between +3.8 and +16.1% for $\delta^{18}O_{SO4}$, with an 670 average value of +7.2% (n = 64) (Table 3, Fig. 6). Most of the groundwater samples fall 671 within the area defined by the isotope signatures of local anthropogenic sources (Table 672 4) showing that SO_4^{2-} in the Baix Ter groundwater can be explained by a ternary mixing 673 between: 1) mineral fertilizers, 2) sewage and 3) pig manure (Fig. 6). This comforts the 674 conclusions from the study of sulphate and nitrate groundwater concentrations. 675 Still, the $\delta^{34}S$ and a $\delta^{18}O_{SO4}$ values measured between 0 and +6‰ of samples $Q_{17},$ 676 T_{11} , T_{18} and T_{21} could indicate a soil origin (Table 4), in agreement with their low SO₄²⁻ 677 concentrations (around 30 mg $SO_4^{2-}L^{-1}$). 678

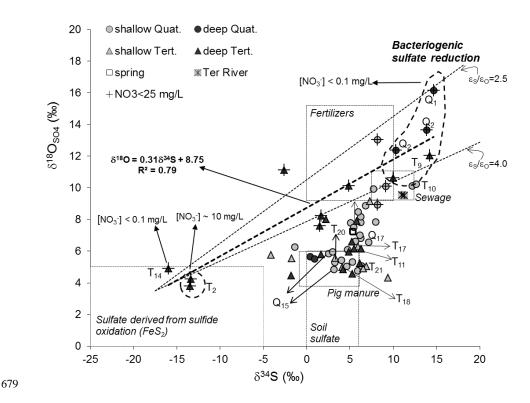


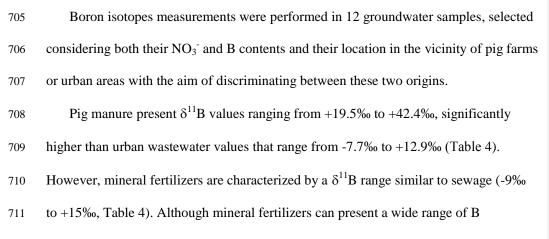
Figure 6. δ^{34} S and δ^{18} O of dissolved SO₄²⁻ in groundwater according to their hydrogeological unit. Isotope ranges of natural and anthropogenic SO₄ sources listed in Table 4 are also represented. The area of sulphates derived from sulphide oxidation is from Van Stempvoort and Krouse (1994). Dashed lines define the isotopic fractionation range (ϵ^{34} S/ ϵ^{18} O_{SO4}) in SO₄ reduction reactions, varying between 2.5 and 4 (Mizutani and Rafter, 1973).

686

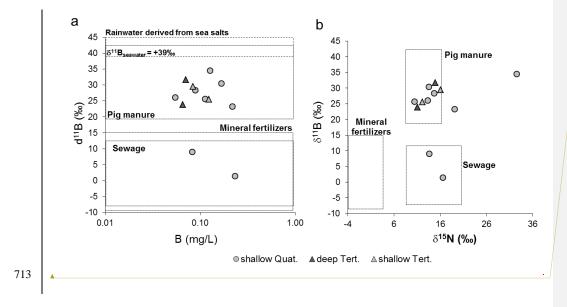
Two sampling sites (T₂ and T₁₄) yielded the lowest negative δ^{34} S values and had 687 $\delta^{18}O_{SO4}$ around +5%, revealing a SO₄²⁻ contribution from a ³⁴S-depleted source of 688 reduced S (Fig. 6). Moreover, both T_2 and T_{14} showed very low (9 mg L⁻¹) or below 689 detection limit (0.1 mg L⁻¹) nitrate concentrations, respectively. On the contrary, 690 samples Q_1 , Q_2 , T_9 and T_{10} , with nitrate concentration below the detection limit (0.1 mg 691 L^{-1}) exhibited the highest δ^{34} S and $\delta^{18}O_{SO4}$ values (+14.7% and +16.1% respectively). 692 All these samples in which nitrate concentration is below detection limit, together 693 with other samples with very low nitrate aqueous concentration (NO₃⁻ < 25 mg L⁻¹) and 694 $\delta^{18}O_{SO4}$ higher than +8% define a linear trend with $\varepsilon_s/\varepsilon_0 = 1/0.31 = 3.2$ compatible with 695 a bacteriogenic reduction of SO_4^{2-} (Mizutani and Rafter, 1973) (Fig. 6). This is 696 consistent with their corresponding low Eh values and high Mn concentrations (Fig. 3). 697 698 However, as the presence of pyrite and gypsum in the area is scarce, autotrophic denitrification can be discarded as the main denitrifying process occurring in the study 699 700 zone. δ^{34} S and $\delta^{18}O_{SO4}$ of the Ter River samples also indicated, in agreement with their 701 δ^{15} N and $\delta^{18}O_{NO37}$ that the dissolved SO₄²⁻ in surface waters originated from 702

703 wastewater.

704 **4.4.3.** δ^{11} **B**

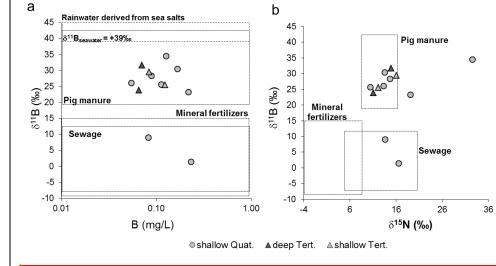


concentrations they usually have lower B contents compared pig manure (Fig. 7a).



Formatted: Font: 12 pt

Formatted: Font: 12 pt



714

Figure 7. δ^{11} B values plotted against B concentration (a) and δ^{15} N values (b). Isotope ranges of the main NO₃⁻ sources listed in Table 4 are also represented. δ^{11} B_{seawater} is taken from Vengosh et al. (1994).

 δ^{11} B composition of dissolved B in selected groundwater samples ranged between 719 720 +1.4% and +34.5%, with an average value of +24.1% (n = 12). B concentrations in these samples ranged between 0.055 and 0.232 mg L⁻¹. No trends or enrichment in δ^{11} B 721 composition of dissolved B with decreasing B content were observed (Fig. 7a). 722 indicating that B is not explained by binary mixing relationships and that no significant 723 724 sorption/desorption processes of B onto/from clay minerals are occurring. Most samples fell in the isotope range of pig manure (Fig. 7a and 7b). This is in agreement with the 725 conclusions drawn from the NO₃⁻ and SO₄²⁻ isotope data. Two of the samples showed 726 δ^{11} B values consistent with a wastewater origin. They correspond to groundwater 727 collected in La Bisbal (Q_{20}) and Ullastret (Q_{21}) water supply wells (Fig. 1), located 728 downstream the discharge of the La Bisbal water treatment plant into the Daró River. 729

Boron analyses, thus, suggest that pig manure is the main source of contamination
and that the influence of sewage and mineral fertilizers is lower than the contribution
from organic residues.

733 **4.4.4.** δ¹³C of HCO₃⁻

Samples presented $\delta^{13}C_{HCO3}$ values between -6.5‰ and -16.2‰ (Table 3). $\delta^{13}C_{HCO3}$ 734 values of marine marls in the study zone are $\delta^{13}C \sim 0\%$. Typical $\delta^{13}C$ values for CO₂ 735 dissolved in the soil are between -14‰ and -16‰; for soil HCO₃⁻ δ^{13} C values are 736 around -23‰ and for pig manure, mineral fertilizers and sewage, $\delta^{13}C$ values range 737 from -23.8‰ to -16.4‰, from -35‰ to -24‰ and from -25‰ to -13‰, respectively 738 (Table 4). 739 Denitrification catalysed by organic matter oxidation induces a decrease in NO_3 740 and in total organic carbon concentrations coupled with an increase in dissolved 741 inorganic carbon concentration (eq.1), causing an increase of δ^{15} N and $\delta^{18}O_{NO3}$ and a 742 decrease in $\delta^{13}C_{HCO3}$ (Faure, 1977). 743 Fig. 8a shows the evolution of the $\delta^{18}O_{NO3}$ as a function of $\ln(NO_3/HCO_3)$. A slight 744 increase in $\delta^{18}O_{NO3}$ coupled to a decrease in $\ln(NO_3^{-}/HCO_3^{-})$ can be observed that would 745 suggest that denitrification may occur. Nevertheless, we were not able to observe the 746 corresponding decrease in $\delta^{13}C_{HCO3}$ in our results (Fig. 8b). As already discussed 747 porewaters presented HCO₃⁻-Ca²⁺-Mg²⁺ facies, with saturation indices for Ca-Mg-748 749 carbonates between -1 and 1. This indicates that bicarbonate is in equilibrium with Ca-Mg-carbonates whose dissolution and precipitation will contribute to the buffering of 750 the $\delta^{13}C_{HCO3}$ of our samples with a final isotope composition corresponding to 751 sedimentary rocks (δ^{13} C around 0 ‰ after Travé et al., 1997). Besides these 752 dissolution/precipitation reactions, $\delta^{13}C_{HCO3}$ can be also affected by other reactions such 753

as equilibrium with $CO_2(g)$ and other sources such as manure or sewage (Clark and

755 Fritz, 1997).

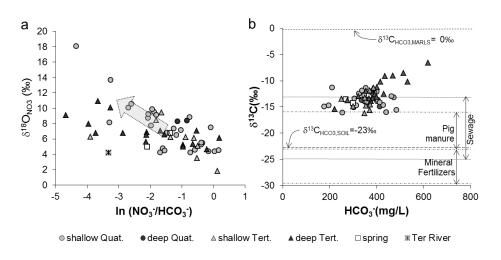




Figure 8. a) $\delta^{18}O_{NO3}$ values plotted against ln(NO₃⁻/HCO₃⁻). b) $\delta^{13}C_{HCO3}$ values plotted against HCO₃⁻ concentration. Isotope ranges of the main NO₃⁻ sources listed in Table 4 are also represented. Value for $\delta^{13}C_{HCO3}$ for marls is from Travé et al. (1997).

760 5. Conclusions

Here we have The coupled the study of hydrochemical and multi-isotope data in 761 relation with the hydrogeological framework information to identify provides a valuable 762 insight into the sources and to characterise processes controlling the budget of dissolved 763 NO₃ in ground- and surface water <u>, even</u> in a complex hydrogeological system (the 764 765 Baix Ter basin).- This approach has proved to be useful in providing both a better identification of the pollution sources and a better description of the natural attenuation 766 767 processes taking place. This is a very valuable information for the design of water quality management policies. 768 IWhen applied to the Baix Ter basin, isotope data have been useful to further define 769 770 shown that the sources of recharge of for both the Tertiary and the Quaternary aquifers are, namely the rainfall, the Ter River in the NW and a contribution from Les Gavarres 771

772	Massif. Moreover, $\frac{it-they}{it-they}$ showed that dissolved NO ₃ ⁻ in groundwater in the study area
773	mainly comes from pig manure application onto the fields, with minor contributions
774	from sewage and mineral fertilizers. The study of $\delta^{11}B$ confirmed pig manure as the
775	main vector of pollution but also identified an urban origin for two of the analysed
776	wells. The dual-isotope (δ^{15} N and δ^{18} O of NO ₃) approach indicated that mineralization-
777	immobilization-turnover (MIT) and natural denitrification processes are occurring
778	within the study area. The δ^{34} S and δ^{18} O of SO ₄ ²⁻ showed that NO ₃ ⁻ reduction is not
779	controlled by the oxidation of pyrites but rather by the oxidation of organic matter.
780	However, the role of organic matter in NO3 ⁻ attenuation could neither be confirmed nor
781	discarded by the study of the $\delta^{13}C_{HCO3}$ as other processes and sources ultimately
782	buffered these isotope compositions. The consumption of organic matter in anaerobic
783	environments is favoured by 1) the river-aquifer connection, 2) the existence of some
784	organic layers in the Ter riversides, and 3) mixing between polluted groundwater and
785	deep regional flows with reducing conditions.
786	Since the role of organic matter in the NO_3^- reduction is still an on-going research,
787	further studies on the $\delta^{13}C$ of local contaminant sources and on the role of MnO_2 should
788	be further investigated. Even if working with samples from exploitation wells, it has
789	been proved that Mmulti-isotope studies allow us to: i) describe groundwater dynamics,
790	ii) discriminate between sources of pollution and determine their relative contribution,
791	iii) characterise the processes affecting the overall nitrogen budget, such as natural
792	attenuation, that in another way would go unnoticed. Still, these approaches highly
793	depend on the knowledge of the isotopic signatures of the different potential sources of
794	nitrate contamination of a given area, on the complexity of the aquifers complex and on
795	the availability of a good infrastructure (e.g. multi-piezometers).
796	

797 Acknowledgements

798	This research was funded by the <u>ATENUATION (CGL2011-29975-C04-01) and</u>
799	REMEDIATION (CGL2014-57215-C4-1-R) projects from Spanish Ministry of
800	Economy and Competitiveness (MINECO) and the AGAUR from the Catalan
801	Government (grant 2014SGR-1456).and CGL2014-57215-C4-1-R from the Spanish
802	Government and project 2014SGR-1456 from Catalan Government. We would like to
803	thank the Centres Científics i Tecnològics of the Universitat de Barcelona for its
804	laboratory help. Authors acknowledge the fruitful comments of the three anonymous
805	reviewers.
806	

807 **References**

808	ACA, 2007. Diagnosis de la causalidad de la contaminación por nitratos de algunos
809	abastecimientos públicos en las zonas vulnerables de Cataluña, análisis de
810	alternativas, medidas de prevención y corrección. Área vulnerable 1 Girona.
811	Estudio 1: Llanura al·luvial de los ríos Ter y Daró, provincia de Girona. ACA
812	(Water Catalan Agency) Internal Report. 168 pp.
813	ACA, 2015. Agència Catalana de l'Aigua. Generalitat de Catalunya. Consulta de dades.
814	Available at: <u>http://aca-web.gencat.cat/aca/appmanager/aca/aca/</u> (June 2016).
815	Altman, S.J., Parizek, R.R., 1995. Dilution of non-point source nitrate in ground water.
816	J. Environ. Qual. 24, 707-718.
817	Amiri, H., Zare, M., Widory. D., 2015. Assessing sources of nitrate contamination in
818	the Shiraz urban aquifer (Iran) using the δ^{15} N and δ^{18} O dual-isotope approach.
819	-Isotopes in Environmental and Health Studies. DOI:
820	10.1080/10256016.2015.1032960.
821	Anderson, K. K., Hooper, A. B., 1983. O ₂ and H ₂ O are each the source of one O in NO ₂
822	produced from NH ₃ by Nitrosomas- ¹⁵ N-NMR evidence. FEBS Letters, 64, 236–
823	40.
824	Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in
825	source identification of nitrate from septic tanks. Ground Water, 31, 180-186.
826	Aravena, R., Robertson, W.D., 1998. Use of Multiple Isotope Tracers to Evaluate
827	Denitrification in Ground Water: Study of Nitrate from a Large-Flux Septic
828	System Plume. Ground Water, 36, 975-982.
829	Aravena, R., Mayer, B., 2010. Isotopes and Processes in the Nitrogen and Sulfur
830	Cycles. In: Aelion, C.M., Höhener, P., Hunkeler, D., Aravena, R. (Eds.),

831	Environmental Isotopes in Biodegradation and Bioremediation. CRC Press, pp.
832	203–246.
833	Archna, Surinder K. Sharma, Ranbir Chander Sobti, 2012. Nitrate Removal from
834	Ground Water: A Review. E Journal of Chemistry, 9, 4, 1667-1675.
835	doi:10.1155/2012/154616.
836	Barroso, M.F., Ramalhosa, M.J., Olhero, A., Antão, M.C., Pina, M.F., Guimarães, L.,
837	Teixeira, J., Alfonso, M.J., Delerue-Matos, C., Chaminé, H.I., 2015. Assessment
838	of groundwater contamination in an aricultural peri-urban area (NW Portugal):
839	an integrated approach. Environ Earth Sci 73, 2881-2894.
840	Basset, R.L., Buszka, P.M., Davidson, G.R., Chong-Diaz, D., 1995. Identification of
841	groundwater solute sources using boron isotopic composition. Environ. Sci.
842	Technol. 29, 2915–2922.
843	Bateman, A.S., Kelly, S.D., 2007. Fertilizer nitrogen isotope signatures. Isotopes in
844	Environmental and Health Studies, 43, 237-247.
845	Borch, T., Kretzschmar, R., Kappler, A., Van Cappellen, P., Ginder-Vogel, M.,
846	Voegelin, A., Campbell, K., 2010. Biogeochemical Redox Processes and their
847	Impact on Contaminant Dynamics. Environmental Science and Technology, 44,
848	15–23.
849	Böttcher, J., Strebel, O., Voerkelius, S., Schmidt, H.L., 1990. Using isotope
850	fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial
851	denitrification in sandy aquifer. Journal of Hydrology, 114, 413-424.
852	Bryan, N.S., Alexander, D.D., Coughlin, J.R., Milkowski, A.L., Boffetta, P., 2012.
853	Ingested nitrate and nitrite and stomach cancer risk: An updated review. Food
854	and Chemical Toxicology, 50, 3646–3665.

855 Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers,
856 New York. 352 pp.

857	Cravotta, C.A., 1997. Use of Stable Isotopes of Carbon, Nitrogen and Sulphur to
858	Identify Sources of Nitrogen in Surface Waters in the Lower Susquehanna River
859	Basin, Pennsylvania. U.S. Geological Survey Water-Supply Paper 2497.
860	Curt, M.D., Aguado, P., Sánchez, G., Bigeriego, M., and Fernández, J., 2004. Nitrogen
861	isotope ratios of synthetic and organic sources of nitrate water contamination in
862	Spain. Water, Air and Soil Pollution, 151, 135-142.
863	Delconte. C.A., Sacchi, E., Racchetti, E., Bartoli, M., Mas-Pla, J., Re, V., 2014.
864	Nitrogen inputs to a river course in a heavily impacted watershed: a combined
865	hydrochemical and isotopic evaluation (Oglio River Basin, N Italy). Science of
866	the Total Environment 466-467, 924-938, DOI: 10.1016/j.scitotenv.2013.07.092.
867	EC (European Communities), 1991. Council Directive 91/676/EC, of 12 December
868	1991, concerning the protection of waters against pollution caused by nitrates
869	from agricultural sources.
870	EC (European Communities), 1998. Council Directive 98/83/EC, of 3 November 1998,
871	on the quality of water intended for human consumption.
872	EC (European Communities), 2000. Directive 2000/60/EC of the European Parliament
873	and of the Council establishing a framework for the Community action in the
874	field of water policy (Water Framework Directive). Official Journal of the
875	European Communities, OJ L 327.
876	EC (European Communities), 2006. Directive 2006/118/EC of the European Parliament
877	and of the Council on the protection of groundwater against pollution and
878	deterioration (Groundwater Directive). Official Journal of the European
879	Communities, OJ L 372.

EEA (European Environment Agency), 1999. Nutrients in European Ecosystems.

- 881 Environmental assessment report Nº 4.
- EEA (European Environment Agency), 2012. European waters: assessment of status
- and pressures. EEA Report Nº 8. Published: Nov 13, 2012. Copenhagen,
- 884 Denmark.
- 885 EEA (European Environment Agency), 2015. Nutrients in freshwater. Indicator
- assessment. Data and maps. IND-8-en. CSI 020, WAT 003. Published: Sep 4th,
- 887 2015. Copenhagen, Denmark. Available as a website at
- 888 <u>http://www.eea.europa.eu/data-and-maps/indicators/nutrients-</u>
- 889 <u>infreshwater/nutrients-in-freshwater-assessment-published-6</u>.
- ⁸⁹⁰ Faure, G. 1997. Principles of isotope geology, Wiley, 2nd Ed, 589 pp.
- Fukada, T., Hiscock, K., Dennis, P.F., Grischek, T., 2003. A dual isotope approach to
 identify denitrification in groundwater at a river-bank infiltration site. Water
- 893 Res. 37, 3070–3078.
- Gaillardet, J., Allègre, C.J., 1995. Boron isotopic compositions of corals: Seawater or
 diagenesis record? Earth and Planetary Science Letters- 136, 665-676.
- Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and
 atmosphere: a review. Chem. Geol. 59, 87–102.
- Hollocher, T. C., 1984. Source of oxygen atoms in nitrate in the oxidation of nitrite by
 Nitrobacter agilis and evidence against a P-O-N anhydride mechanism in
- 900 oxidative phosphorylation. Archives of Biochemistry and Biophysics, 233, 721–
 901 27.
- Horibe, Y., Shigehara, K., Takakuwa, Y., 1973. Isotope separation factors of carbon
- dioxide-water system and isotopic composition of atmospheric oxygen. Journal
- 904 of Geophysical Research, 78, 2625-2629.

905	Ishikawa, T., Nakamura, E., 1990. Suppression of boron volatilization from a
906	hydrofluoric acid solution using a boron-mannitol complex., Analytical
907	Chemistry 62, 2612–2616.
908	Jurado, A., Vàzquez-Suñé, E., Soler, A., Tubau, I., Carrera, J., Pujades, E., Anson, I.,
909	2013. Application of multi-isotope data (O, D, C and S) to quantify redox
910	processes in urban groundwater. Applied Geochemistry, 34, 114-125.
911	Karr, J.D., Showers, W.J., Wendell Gilliam, J., Scott Andres, A., 2001. Tracing nitrate
912	transport and environmental impact from intensive swine farming using delta
913	nitrogen-15. J. Environ. Qual. 30, 1163-1175.
914	Kendall, C., 1998. Tracing Nitrogen Sources and Cycling in Catchments. In: Isotope
915	Tracers in Catchment Hydrology, C. Kendall and J. J. McDonnell (Eds.).
916	Elsevier Science B.V., Amsterdam, 839 p., 519-576.
917	Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen
918	to ecosystems, Chapter 12. In: R.H. Michener and K. Lajtha (Eds.), Stable
919	Isotopes in Ecology and Environmental Science, 2nd edition, Blackwell
920	Publishing, pp. 375-449.
921	Koba, K., Tokuchi, N., Wada, E., Nakajima, T., Iwatsubo, G., 1997. Intermittent
922	denitrification: the application of a ¹⁵ N natural abundance method to a forested
923	ecosystem. Geochim. Cosmochim. Acta, 61, 5043-5050.
924	Komor, S.C., 1997. Boron contents and isotopic compositions of hog manure, selected
925	fertilizers, and water in Minnesota. J. Environ. Qual. 26, 1212–1222.
926	Krouse, H.R., Mayer, B., 2000. Sulphur and oxygen isotopes in sulphate. In: Cook,
927	P.G., Hercseg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology.
928	Kluwer Academic Press, Boston, pp. 195–231.

929	Li, X-2D, Liu, C-Q, Harue, M., Li, S-L, Liu, X-L, 2010. The use of environmental
930	isotopic (C, Sr, S) and hydrochemical tracers to characterize anthropogenic
931	effects on karst groundwater quality: A case study of the Shuicheng Basin, SW
932	China. Applied Geochemistry, 25, 1924–1936.
933	Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, P., 1981.
934	Experimental determination of nitrogen kinetic isotope fractionation: some
935	principles, illustration for the denitrification and nitrification processes. Plant
936	Soil, 62, 413–430.
937	Mariotti, A., Landreau, A., Simon, B., 1988. ¹⁵ N isotope biogeochemistry and natural
938	denitrification process in groundwater: application to the chalk aquifer of
939	northern France. Geochim. Cosmochim. Acta, 52, 1869–1878.
940	Mas-Pla, J., Bach, J., Montaner J., 1998. Distribución de la concentración de nitratos en
941	el sistema hidrogeológico Baix Ter-Gavarres (Girona). In: La contaminación de
942	las aguas subterráneas: Un problema pendiente. ITGE-AIH, pp. 139–145.
943	Mas-Pla, J., Vilanova, E., 2001. Dinámica del sistema hidrogeológico Baix Ter-
944	Gavarres en base a isótopos estables. In: IGME, Las Caras del Agua, Serie
945	Hidrogeología y Aguas Subterráneas n. 1/2001, tomo I, pp. 395-402.
946	Menció, A., J. Mas-Pla, A. Soler, N. Otero, O. Regàs, M. Boy-Roura, R. Puig, J. Bach,
947	C. Domènech, A. Folch, M. Zamorano, D. Brusi (2016). Nitrate pollution of
948	groundwater; all right, but nothing else? Science of the Total Environment,
949	539C: 241-251. DOI: 10.1016/j.scitotenv.2015.08.151
950	Mengis, M., Walther, U., Bernasconi, S.M., Wehrli, B., 2001. Limitations of using $\delta^{18}O$
951	for the source identification of nitrate in agricultural soils. Environ. Sci. Technol.
952	35 (9), 1840–1844.

953	Michalski, G., Kolanowski, M. Rihaa, K.M., 2015. Oxygen and nitrogen isotopic
954	composition of nitrate in commercial fertilizers, nitric acid, and reagent salts.
955	Isotopes in Environmental and Health Studies 51, 382-391.
956	Mizutani, Y., Rafter, T.A., 1973. Isotopic behaviour of sulphate oxygen in the bacterial
957	reduction of sulphate. Geochemical Journal, 6, 183-191.
958	Montaner, J., Pons, P., López, J., 2010. Caracterització del flux hidrològic a la plana
959	litoral del Baix Ter. In: El flux hidrològic de la plana litoral del Baix Ter.
960	Evolució fluvial, caracterització hidrològica i pautes de gestió. Montaner, J.
961	(coord.). Càtedra d'Ecosistemes Litorals Mediterranis. Museu de la Mediterrània
962	(Ed.). Recerca i Territori, 2.
963	Neal, C., Neal, M., Warrington, A., Àvila, A., Piñol, J., Rodà, F., 1992. Stable hydrogen
964	and oxygen isotope studies of rainfall and streamwaters for two contrasting holm
965	oak areas of Catalonia, northeastern Spain. Journal of Hydrology, 140, 163-178.
966	Otero, N., Canals, A., Soler, A., 2007. Using dual-isotope data to trace the origin and
967	processes of dissolved sulphate: a case study in Calders stream (Llobregat basin,
968	Spain). Aquat. Geochem. 13, 109–126.
969	Otero, N., Soler, A., Canals, A., 2008. Controls of δ^{34} S and δ^{18} O in dissolved sulphate:
970	Learning from a detailed survey in the Llobregat River (Spain). Applied
971	Geochemistry, 23, 1166-1185.
972	Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J., 2009. Monitoring
973	groundwater nitrate attenuation in a regional system coupling hydrogeology with
974	multi-isotopic methods: the case of Plana de Vic (Osona, Spain). Agr. Ecosyst.
975	Environ. 133 (1-2), 103–113.

976	Panno, S.V., Hackley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the
977	sources of nitrate contamination in karst springs using isotopic and chemical
978	indicators. Chemical Geology, 179, 113-128.
979	Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate
980	attenuation in groundwater: a review of biogeochemical controlling processes.
981	Water Res. 42, 4215–4232.
982	Rock, L., Mayer, B., 2002. Isotopic assessment of sources and processes affecting
983	sulphate and nitrate in surface water and groundwater of Luxembourg. Isotopes
984	Environ. Health Stud. 38 (4), 191-206.
985	Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte. C.A., Laini, A., Pennisi, M.
986	(2013) Origin and fate of nitrates in groundwater from the central Po plain:
987	Insights from isotopic investigations. Applied Geochemistry 34, 164-180.
988	Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Böttcher, M.E., Savarino, J.,
989	Escher, P., Eisenhauer, A., Erbland, J., 2013. Multi-isotope approach for the
990	identification and characterization of nitrate pollution sources in the Marano
991	lagoon (Italy) and parts of its catchment area. Appl. Geochem., 34, 75-89.
992	Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., Mariotti, A., 2013. Long-term fate of
993	nitrate fertilizer in agricultural soils. PNAS (Proceedings of the National
994	Academy of Sciences of the United States of America).
995	www.pnas.org/cgi/doi/10.1073/pnas.1305372110
996	Seiler, R. L., 2005. Combined use of ¹⁵ N and ¹⁸ O of nitrate and ¹¹ B to evaluate nitrate
997	contamination in groundwater. Applied Geochemistry, 20, 1626-1636.
998	Silva, S.R., Ging, P.B., Lee, R.W., Ebbert, J.C., Tesoriero, A.J., Inkpen, E.L., (2002)
999	Forensic applications of nitrogen and oxygen isotopes in tracing nitrate sources

1000	in urban environments. Environ Forensic 3, 125–130.
1001	doi:10.1006/enfo.2002.0086.
1002	Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., Avanzino, R.J.,
1003	2000. A new method for collection of nitrate from fresh water and the analysis
1004	of nitrogen and oxygen isotope ratios. Journal of Hydrology, 228, 22-36.
1005	Spivack, A.J., Edmond, J.M., 1986. Determination of boron isotope ratios by thermal
1006	ionization mass spectrometry of the dicesium metaborate cation. Anal. Chem.,
1007	58, 31-35.
1008	Tirez, K., Brusten, W., Widory, D., Petelet, E., Bregnot, A., Xue, D., Boeckx, P.,
1009	Bronders, J., 2010. Boron Isotope Ratio ($\delta^{11}B$) Measurements in Water
1010	Framework Directive Programs: Comparison between Double Focusing Sector
1011	Field ICP and Thermal Ionization Mass Spectrometry, J. Anal. At. Spectrom. 25,
1012	964-974.
1013	Travé, A., Labaume, P., Calvet, F., Soler, A. (1997) Sediment dewatering and pore fluid
1014	migration along thust faults in a foreland basin inferred from isotopic and
1015	elemental geochemical analyses (Eocene southern Pyrenees, Spain).
1016	Tectonophysics 282, 375-398.
1017	Vane, C.H., Kim, A.W., McGowan, S., Leng, M.J., Heaton, T.H.E., Kendrick, C.P.,
1018	Coombs, P., Yang, H., Swann, G.E.A., 2010. Sedimentary records of sewage
1019	pollution using faecal markers in contrasting peri-urban shallow lakes. The
1020	Science of the Total Environment 409, 345-356.
1021	Van Stempvoort, D.R., Krouse, H.R., 1994. Controls of δ^{18} O in sulphate. In: Alpers,
1022	C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulphide Oxidation.
1023	American Chemical Society, Washington, pp. 446–480.

1024	Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron Isotope Application
1025	for Tracing Sources of Contamination in Groundwater. Environmental, Science
1026	and Technology 28, 1968-1974.
1027	Vilanova, E., 2004. Anàlisi dels sistemes de flux a l'àrea Gavarres-Selva-Baix
1028	Empordà. Proposta de model hidrodinàmic regional. Ph.D Dissertation.
1029	Universitat Autònoma de Barcelona, 337 pp.
1030	http://www.tdx.cat/handle/10803/3437
1031	Vilanova, E., Mas-Pla, J., 2004. Identificación de sistemas de flujo en base a datos
1032	isotópicos en el área Gavarres-Baix Empordà-Selva (CIC). Geotemas, 6(4), 197-
1033	202.
1034	Vilanova, E., Mas-Pla, J., Menció, A., 2008. Determinación de sistemas de flujo
1035	regionales y locales en las depresiones tectónicas del Baix Empordà y La Selva
1036	(NE de España) en base a datos hidroquímicos e isotópicos. Boletín Geológico y
1037	Minero, 119 (1), 51-62.
1038	Vitòria, L., 2004. Estudi multi-isotòpic (δ^{15} N, δ^{34} S, δ^{13} C, δ^{18} O, δ D i 87 Sr/ 86 Sr) de les
1039	aigües subterrànies contaminades per nitrats d'origen agrícola i ramader.
1040	Translated title: Multi-isotopic approach ($\delta^{15}N$, $\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$, δD and
1041	⁸⁷ Sr/ ⁸⁶ Sr) of nitrate contaminated groundwaters by agricultural and stockbreeder
1042	activities. PhD Thesis. Universitat de Barcelona, 188 pp.
1043	Vitòria, L., Otero, N., Canals, A., Soler, A., 2004. Fertilizer characterization: isotopic
1044	data (N, S, O, C and Sr). Environ. Sci. Technol. 38, 3254–3262.
1045	Vitòria, L., Soler, A., Aravena, R., Canals, A., 2005. Multi-isotopic approach (¹⁵ N, ¹³ C,
1046	³⁴ S, ¹⁸ O and D) for tracing agriculture contamination in groundwater (Maresme,
1047	NE Spain). In: Environmental Chemistry (Eds. E. Lichtfouse, J. Schwarzbauer
1048	and D. Robert). Springer-Verlag, Heidelberg, 43-56.

1049	Vitòria, L., Soler, A., Canals, A., Otero, N., 2008. Environmental isotopes (N, S, C, O,
1050	D) to determine natural attenuation processes in nitrate contaminated waters:
1051	example of Osona (NE Spain). Appl. Geochem. 23, 3597-3611.
1052	Waldron, S., Tatner, P., Jack, I., Arnott, C., 2001. The Impact of Sewage Discharge in a
1053	Marine Embayment: A Stable Isotope Reconnaissance. Estuarine, Coastal and
1054	Shelf Science, 52, 111–115. doi:10.1006/ecss.2000.0731.
1055	Ward, M.H., deKok, T.M., Levallois, P., Brender, J., Gulis, G., Nolan, B.T.,
1056	VanDerslice, J., 2005. Workgroup report: drinking-water nitrate and health-
1057	recent findings and research needs. Environ. Health Perspect. 113, 1607-1614.
1058	Wassenaar, L. I., 1995. Evaluation of the origin and fate of nitrate in the Abbotsford
1059	aquifer using the isotopes of 15 N and 18 O in NO ₃ . Applied Geochemistry, 10,
1060	391–405.
1061	Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J.L., 2004.
1062	Nitrate in groundwater: an isotopic multi-tracer approach. Journal of
1063	Contaminant Hydrology, 72, 165-188.
1064	Widory, D., Petelet-Giraud, E., Négrel, P., Ladouche, B., 2005. Tracking the sources of
1065	nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis.
1066	Environmental, Science and Technology, 39, 539-548.
1067	Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2013.
1068	Improving the management of nitrate pollution in water by the use of isotope
1069	monitoring: the $\delta^{15}N$, $\delta^{18}O$ and $\delta^{11}B$ triptych. Isotopes in Environmental and
1070	Health Studies, 48, 1-19.
1071	Xu, S., Kang, P., Sun, Y., 2016. A stable isotope approach and its application for
1072	identifying nitrate source and transformation process in water. Environ Sci
1073	Pollut Res 23, 1133-1148.

1074	Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O.,
1075	Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of
1076	stable isotope methods for nitrate source identification in surface- and
1077	groundwater. Water Research, 43, 1159-1170.
1078	Yingkai, X., Lan, W., 2001. The effect of pH and temperature on the isotopic
1079	fractionation of boron between saline brine and sediments. Chem. Geol. 171,
1080	253–261.

1082 Figure captions

1083	Figure 1. Geological map of the Baix Ter basin, sampling point locations labelled
1084	according to the hydrogeological formation where they are located. Potentiometric
1085	contour lines of the unconfined aquifer, mainly in the shallow Quaternary formations,
1086	correspond to the August 2004 survey. Dashed line represents the zero elevation
1087	potentiometric level in the deep quaternary formations (mainly leaky aquifers) affected
1088	by intensive withdrawal rates in the central area of the basin. Geology from ICGC
1089	(http://www.icgc.cat).Figure 1. Baix Ter basin map showing the geology and sampling
1090	points, labelled according to their hydrogeological formation (round and triangle shapes
1091	distinguish between Quaternary and Tertiary aquifers, respectively, and light and bold
1092	points, between shallow and deep formations, respectively; square refers to the sampled
1093	spring). Potentiometric contour lines correspond to the water table measurements of the
1094	Quaternary unit (August 2004).
1095	
1096	Figure 2. $\delta^{18}O_{H2O}$ and $\delta^{2}H$ of the Baix Ter groundwater samples collected in January
1097	2004 (a) and August 2004 (b). The annual-Local Meteoric Water Line (LMWL) follows
1098	the equation $\delta^2 H = 7.98(\pm 2.71) \delta^{18}O + 7.85(\pm 0.47)$ (r ² =0.924, n=23) (Vilanova, 2004),
1099	whose slope is equal to that of the neighbouring areas ($\delta^2 H = 7.9 \ \delta^{18} O + 9.8$; Neal et al.,
1100	1992).
1101	
1102	Figure 3. Mn concentrations plotted against the Eh values of the groundwater samples.

- Eh ranges of MnO_2/Mn^{2+} and $NO_3^{-}/N_{2(g)}$ redox pairs are taken from Rivett et al. (2008).
- 1104

1105	Figure 4 a) NO ₃ ⁻ concentration versus Cl ⁻ concentration, b) NO ₃ ⁻ concentration versus
1106	SO_4^{2-} concentration, c) SO_4^{2-} concentration versus (NO ₃ ⁻ /Cl ⁻) ratio, and d) B
1107	concentration versus (NO_3^{-}/Cl^{-}) ratio.
1108	
1109	Figure 5. a) Variations of the δ^{15} N and δ^{18} O of dissolved NO ₃ in groundwater according
1110	to their hydrogeological unit. Isotope ranges of the main NO ₃ sources listed in Table 4
1111	are also represented. The extreme isotopic fractionation ratiosfactors from the literature
1112	are $\varepsilon_{N}/\varepsilon_{O} = 2.1$ (Böttcher et al., 1990) and $\varepsilon_{N}/\varepsilon_{O} = 1.3$ (Fukada et al., 2003). b) $\delta^{18}O_{NO3}$
1113	values plotted against ln(NO3 ⁻ /Cl ⁻) according to their hydrogeological unit. R ² values
1114	offor the linear regressions for shallow Quat. and deep Tert. Units are also reported.
1115	Variations of the δ^{15} N and δ^{18} O of dissolved NO ₃ in groundwater according to their
1116	hydrogeological unit. Isotope ranges of the main NO3 ⁻ sources listed in Table 4 are also
1117	represented. The extreme isotopic fractionation ratios from the literature are $\epsilon_N/\epsilon_0 = 2.1$
1118	(Böttcher et al., 1990) and $\varepsilon_N/\varepsilon_0 = 1.3$ (Fukada et al., 2003).
1119	
1120	Figure 6. δ^{34} S and δ^{18} O of dissolved SO ₄ ²⁻ in groundwater according to their
1121	hydrogeological unit. Isotope ranges of natural and anthropogenic SO ₄ sources listed in
1122	Table 4 are also represented. The area of sulphates derived from sulphide oxidation is
1123	from Van Stempvoort and Krouse (1994). Dashed lines define the isotopic fractionation

range (ϵ^{34} S/ ϵ^{18} O_{SO4}) in SO₄ reduction reactions, varying between 2.5 and 4 (Mizutani and Rafter, 1973).

1126

Figure 7. δ^{11} B values plotted against B concentration (a) and δ^{15} N values (b). Isotope ranges of the main NO₃⁻ sources listed in Table 4 are also represented. δ^{11} B_{seawater} is taken from Vengosh et al. (1994).

1131	Figure 8. a) $\delta^{18}O_{NO3}$ values plotted against ln(NO ₃ ⁻ /HCO ₃ ⁻). b) $\delta^{13}C_{HCO3}$ values plotted
1132	against HCO_3^- concentration. Isotope ranges of the main NO_3^- sources listed in Table 4
1133	are also represented. Value for $\delta^{13}C_{HCO3}$ for marls is from Travé et al. (1997).
1134	
1135	Table captions
1136	Table 1. Hydrogeological formation, X and Y UTM coordinates, depth (m), hydraulic
1137	head (m.a.s.l.), and physico-chemical parameters measured in situ for the sampled
1138	points of each field campaign. See Fig. 1 for sampling locations in the Baix Ter basin.
1139	R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig.
1140	1). (<i>n.d.</i> : Not determined).
1141	
1142	Table 2. Hydrochemical data for the January and August 2004 field campaigns ("*" =
1143	DOC concentrations instead of TOC concentrations). R_1 and R_2 Ter River samples are
1144	from the Colomers station, NW of the study zone (Fig. 1). (n.d.: Not determined; u.d.l.:
1145	under detection limit).
1146	
1147	Table 3. Isotope data for the January and August 2004 field campaigns. R_1 and R_2 Ter
1148	River samples are from the Colomers station, NW of the study zone (Fig. 1). (n.d.: Not
1149	determined).
1150	
1151	Table 4. Ranges of nitrate, sulphate, boron and dissolved inorganic carbon isotope
1152	compositions of the main potential sources of nitrate obtained from the literature.
1153	

Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer system (NE Spain) using a multi-isotope approach

Roger Puig^a, Albert Soler^a, David Widory^b, Josep Mas-Pla^{c, d}, Cristina Domènech^a and Neus Otero^a

^aGrup de Mineralogia Aplicada i Geoquímica de Fluids, Dept. de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), c/ Martí i Franquès s/n, 08028 Barcelona, Spain.

^bDépartement des Sciences de la Terre et de l'Atmosphère, Geotop/UQAM, Montréal, Canada.

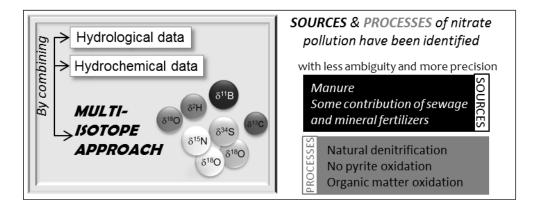
[°]Grup de Geologia Aplicada i Ambiental, Centre de Geologia i Cartografia Ambiental, Dept. de

Ciències Ambientals, Universitat de Girona, 17003 Girona, Spain.

^dCatalan Institute for Water Research, c/ Emili Grahit 101, 17003 Girona, Spain.

Corresponfing author: Cristina Domenech (cristina.domenech@ub.edu)

Graphical abstract



Highlights

- $\delta^{15}N$, $\delta^{18}O_{NO3}$ and $\delta^{11}B$ confirm pig manure as the main vector of NO₃-pollution.
- SO₄²⁻ and B isotopes indicate also contributions from sewage and mineral fertilizers.
- NO_3^- isotopes show that NO_3^- undergoes natural attenuation.

- SO_4^{2-} isotopes confirm that denitrification is not controlled by pyrite oxidation.
- The multi-isotope approach provides a unique and comprehensive approach that allows to characterise the origin of NO₃⁻ pollution as well as the processes involved.

Abstract

Nitrate pollution is a widespread issue affecting global water resources with significant economic and health effects. Knowledge of both the corresponding pollution sources and of processes naturally attenuating them is thus of crucial importance in assessing water management policies and the impact of anthropogenic activities. In this study, an approach combining hydrodynamic, hydrochemical and multi-isotope systematics (8 isotopes) is used to characterise the sources of nitrate pollution and potential natural attenuation processes in a polluted basin of NE Spain. δ^2 H and δ^{18} O isotopes were used to further characterize the sources of recharge of the aquifers. Results show that NO₃⁻ is not homogeneously distributed and presents a large range of concentrations, from no NO₃⁻ to up to 480 mg L⁻¹. δ^{15} N and δ^{18} O of dissolved NO₃⁻ identified manure as the main source of nitrate, although sewage and mineral fertilizers can also be isotopically detected using boron isotopes (δ^{11} B) and δ^{34} S and δ^{18} O of dissolved sulphate, respectively. The multi-isotope approach proved that natural denitrification is occurring, especially in near-river environments or in areas hydrologically related to fault zones. δ^{34} S and δ^{18} O indicated that denitrification is not driven by pyrite oxidation but rather by the oxidation of organic matter. This could not be confirmed by the study of $\delta^{13}C_{HCO3}$ that was buffered by the entanglement of other processes and sources.

Keywords

Stable isotopes, nitrate contamination, boron, denitrification, groundwater, manure

1. Introduction

Nitrate (NO₃⁻) contamination of groundwater is a problem affecting groundwater quality worldwide (Xu et al., 2016 and references therein) that has proved to affect human health (Bryan et al., 2012; Ward et al., 2005). Because of this, considerable efforts have been made by the European authorities to promote both the reduction of NO₃⁻ inputs and the enhancement of attenuation processes in groundwater.

However, no decreasing trends in average European nitrate concentration in groundwater have been observed during the last 15 years (EEA, 2015). Thus, NO₃ concentrations in groundwater often exceed the 50 mg L⁻¹ legal guideline set for drinking water (EC, 1998). NO₃ is currently one of the main contaminants that may hinder achieving the goals of the Water Framework (EC, 2000) and of the European Groundwater (EC, 2006) directives. This arises the need for a better knowledge on the overall nitrogen, including nitrate species cycle in surface water and groundwater.

Nitrogen is mainly incorporated into the soil as a nutrient through mineral fertilizers or manure, each of these sources accounting for nearly 50% of the N input into the European agricultural soils (EEA, 2012). However, other minor N sources such as the leakage of sewage from sewer networks in urban environments (Aravena and Mayer, 2010; Barroso et al., 2015; Sacchi et al., 2013; Vane et al., 2010) have been reported for groundwater.

Once in the soil, nitrogen is transformed through microbially mediated redox reactions (nitrogen fixation, nitrification, denitrification, dissimilatory NO_3^- reduction to ammonium, anammox; Borch et al., 2010). Nitrification represents the oxidation of nitrogen (under the form of ammonia) into nitrate. It frequently occurs in the unsaturated zone where oxygen is available and explains why most of the nitrogen that

reaches groundwater appears as NO_3^{-} . Denitrification is the transformation of nitrate into $N_2(g)$. It is considered the main natural process attenuating nitrate concentration in groundwater. This requires the presence of denitrifying bacteria and electron donors (organic carbon, reduced sulphur and/or reduced iron), abundant presence of NO_3^{-} and an anaerobic environment (Koba et al., 1997; Rivett et al., 2008). Denitrification can be heterotrophic if linked to the oxidation of an organic compound (eq.1) or autotrophic, if linked to the oxidation of an inorganic compound, such as iron sulphide (eq.2).

$$4NO_3^{-} + 5CH_2O \rightarrow 2N_2 + 4HCO_3^{-} + CO_2 + 3H_2O$$
(1)

$$14NO_3^- + 5FeS_2 + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O$$
 (2)

Dilution and dispersion are other processes that can result in a decrease of groundwater nitrate concentration, but contrarily to natural attenuation they do not lead to the mass-reduction of the contaminant within the aquifer.

Knowledge of both the sources of nitrogen contamination and the processes affecting nitrogen once in the aquifer is thus of the utmost importance to better design strategies to ultimately decrease nitrate pollution. The study of the isotope composition of nitrogen compounds has proved to be a viable tool to tackle both issues (e.g. Amiri et al. 2016; Vitòria et al. 2008). Denitrification reactions (eq.1 and 2) affect the isotope composition of the residual nitrate leading to an enrichment in its heavy isotopes ¹⁵N and ¹⁸O (Aravena and Robertson, 1998; Fukada et al., 2003; Kendall et al., 2007; Mariotti et al., 1988). The study of the δ^{15} N and δ^{18} O isotope compositions and nitrate concentrations (eq. 3 and 4) allow to determine the corresponding isotopic enrichment factor (ϵ), used to characterise the extension of the attenuation processes (Böttcher et al., 1990; Fukada et al., 2003; Mariotti et al., 1981). Also, as the initial NO₃⁻ isotope compositions differ between the different nitrate sources (inorganic fertilizers, manure, soil, ...), the δ^{15} N and δ^{18} O compositions of nitrate have been used to identify its origin in groundwater (Aravena et al., 1993; Aravena and Mayer, 2010; Clark and Fritz, 1997; Kendall et al., 2007; Panno et al., 2001).

$$\delta^{15} N_{\text{residual}} = \delta^{15} N_{\text{initial}} + \varepsilon_{N} \ln \left([NO_{3}^{-}]_{\text{residual}} / [NO_{3}^{-}]_{\text{initial}} \right)$$
(3)
$$\delta^{18} O_{\text{residual}} = \delta^{18} O_{\text{initial}} + \varepsilon_{O} \ln \left([NO_{3}^{-}]_{\text{residual}} / [NO_{3}^{-}]_{\text{initial}} \right)$$
(4)

However, in areas characterized by complex groundwater flow systems and exposed to multiple sources of nitrogen, the use of the sole δ^{15} N and δ^{18} O of NO₃⁻ and nitrate concentrations may result in not conclusive results.

To overcome this difficulty, as the redox transformations affecting nitrate also affect the electron donor, some authors have coupled δ^{15} N and δ^{18} O of NO₃⁻ data with the isotope composition of the electron donors or with other types of hydrochemical data, such as conservative elements (Xu et al., 2016). Some authors combined chloride concentration (a conservative element) with δ^{15} N and δ^{18} O of NO₃⁻ to identify nitrate sources and transformation processes (Silva et al. 2002, Vitòria et al. 2008). Some others used the δ^{34} S and δ^{18} O of sulphate or $\delta^{13}C_{HCO3}$ to evaluate if sulphide or organic matter oxidation processes could be linked to denitrification processes (Aravena and Robertson, 1998; Otero et al., 2009; Rock and Mayer, 2002; Saccon et al., 2013; Vitòria et al. 2005, 2008).

Moreover, in the last decade, some studies have also used the isotope composition of boron (δ^{11} B) in combination with the δ^{15} N and δ^{18} O of NO₃⁻ to trace the origin of NO₃⁻ in water (Delconte et al., 2014; Komor, 1997; Saccon et al., 2013; Seiler, 2005; Widory et al., 2004, 2005, 2013). B is usually found in natural ground- and surface water as a minor constituent (<0.05 mg B L⁻¹) whereas contaminant sources are enriched in B (>0.1 mg B L⁻¹; Tirez et al., 2010). Besides the fact that groundwater affected by anthropogenic activities may present elevated B contents (Vengosh et al., 1994), δ^{11} B values are significantly discriminated between manure and wastewater. As for nitrate isotopic composition, δ^{11} B of dissolved B can be modified by different processes. However, the processes that can shift B isotopic composition are aquifer matrix interaction (dissolution of B-bearing silicates) and adsorption-desorption interactions with clay minerals, iron and aluminium oxide surfaces, and/or organic matter (Yingkai and Lan, 2001). No effects on δ^{11} B composition are caused by volatilization and oxidation-reduction reactions (Bassett et al., 1995). Thus, the incorporation of δ^{11} B in the multi-isotope approach of nitrate polluted areas may be useful for a better identification of NO₃⁻ sources (manure or sewage), especially in semirural zones where agricultural and farming practices cohabitate with industrial and urban activities.

However, to our knowledge no study trying to combine these chemical/isotope approaches has ever been reported so far. Here, we aim at assessing the validity of a multi-parameter approach in which, besides the classical δ^{15} N and δ^{18} O of NO₃⁻, hydrochemical data (e.g. Cl⁻ concentration), δ^2 H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulphate, δ^{13} C of HCO₃⁻ and δ^{11} B of dissolved B are used simultaneously to both identify the sources of contamination and to characterise processes affecting the nitrate budget of a given watershed. This study was undertaken in the Baix Ter aquifer (NE Spain), declared vulnerable to NO₃⁻ pollution in 1998 by the local government following the 91/676/EC European Nitrate Directive (EC, 1991). NO₃⁻ contents in groundwater exceeds the 50 mg NO₃⁻ L⁻¹ threshold (ACA, 2007) due to the large amount of fertilizers used by local agriculture (Mas-Pla et al., 1998; Montaner et al. 2010) and pig raising practices that started in the 80's and intensified during the last decades (ACA, 2007; EEA, 1999). This aquifer is subjected to several anthropogenic pressures such as additional nitrate sources or groundwater exploitation that increases the complexity of the aquifer behaviour.

2. Study area

The Baix Ter basin is located in the Baix Empordà tectonic basin (NE Catalonia, Spain) (Fig. 1). The study zone encompasses a 200 km² area characterized by the Ter River alluvial plain delimited by the Montgrí Range to the north (Mesozoic limestone formations) and by the Gavarres Range to the south (Paleozoic igneous and metamorphic rocks) that turns into a fluvio-deltaic environment in its eastern margin. The foothills of the Gavarres Range, as well as the basin basement present Paleogene sedimentary materials (sandstone and limestone formations) that are severely affected by fractures (Mas-Pla and Vilanova, 2001).

The Baix Empordà basin was formed during the distensive period of the Alpine orogenesis. Detritic, fine-grained and silty formations were sedimented during the Neogene. The Quaternary fluvio-deltaic deposits originated from the Ter River as well as from some minor tributaries from the Gavarres Range (i.e., Daró River, Fig. 1). They constitute the main aquifers of the area, and lay on the Neogene sediments in the western area, and on the Paleogene in the eastern part of the basin. Fluvial deposits reach a maximum depth of 50-60 m in the central part of the basin and are constituted by three main distinguishable units according to the Holocene sedimentary sequence (Montaner et al. 2010): a deep level formed by alluvial coarse detritic material, gravel and sand; an intermediate level, formed by sandy lenticular bodies in a silty-sandy level; and a shallow level, mainly sandy formed by the present prograding alluvial deposits that transform into marsh and coastal deposits near the coast line.

Because of this lithological diversity, three distinct aquifer units are differentiated, from bottom to top: a leaky aquifer formed by the deeper coarse sediment layer, a leaky aquifer formed by the intermediate sandy layer, and an upper unconfined aquifer formed by the prograding deposits. All of them present significant lateral variations, especially the upper aquifer that reflects the fluvio-deltaic, marsh and coastal areas presently occurring in the plain. These aquifer units are separated by loamy layers that constitute low permeability units that act as aquitards. Nevertheless, all three aquifer layers overlap in the westernmost part of the area, between Colomers and Verges.

According to Montaner et al. (2010) these aquifers are mainly recharged by local precipitation, seasonal contribution from the Ter and Daró rivers (whether natural or induced by pumping), and by irrigation returns. Moreover, igneous and metamorphic rocks at the Gavarres Range act as regional recharge areas that discharge into the fluvio-deltaic Quaternary aquifers through the preferential upward vertical flow paths of the limestone and carbonate Paleogene aquifers and, more importantly, through the fractures that affect them. Potentiometric, hydrochemical and isotope data indicate that these different aquifers are hydraulically connected (Vilanova et al., 2008).

Potentiometric maps reveal an influent (losing stream) behaviour of the Ter River in its western reach, between Colomers and Verges, and an effluent (gaining stream) behaviour of the Ter and Daró rivers downstream of Verges down to the coast line. However, intense groundwater withdrawal from these aquifers started in the 60's with the agricultural and touristic development of the area that modified the natural flow field causing a noticeable depression cone in the centre of the formation, between the villages of Gualta and Torroella de Montgrí (Fig. 1). This cone creates a downward flow from the upper unconfined aquifer, also capturing the Ter River discharge, which recharges the supply wells located in the lower aquifer levels. The total groundwater abstraction is around 21 hm³/yr, from which 62% are for domestic use (including the touristic season), 36% for agriculture activities and 2% for the industry (ACA, 2007).

The Baix Ter basin area supports rural agriculture and livestock activities, industrial activities and several small to medium-sized urban areas that drastically increase their

population during summer due to their intense touristic activity. About 60% of the surface is covered by herbaceous dry-farmed and irrigated crops (mainly maize, sunflower and rice), 20% by forest and pasture and 7% by fruit growing (ACA, 2007).

The total nitrogen produced by livestock in the study zone is around 500 tons of N year⁻¹. 60% of this amount are from intensive pig rising (460 pigs/km²; 50 m³ ha⁻¹ year⁻¹ of pig manure are applied onto maize crops; ACA, 2007). However, leakage from manure ponds or inappropriate spillages may also contribute to the increase of nitrogen, which is unassimilated by crops and incorporated into the saturated zone, ultimately raising NO₃⁻ concentrations in the groundwater. The "La Bisbal" water treatment plant discharges downstream of Daró River and produces mud that is eventually applied onto the fields, although some corrective measures were adopted to avoid wastewater spills.

3. Methodology

3.1. Sampling

Two sampling campaigns were conducted in the right bank alluvial plain of the Baix Ter basin in January 2004 (24 wells) and in August 2004 (40 wells) to cover both the wet season with fertilization and growing of dry land cereals and the dry season with cultivation of spring cereals, respectively.

All samples were taken from private wells supplied by the shallow Quaternary hydrogeological formation and the upper unconfined aquifer (Q_S), in the deep Quaternary formation and the lower unconfined aquifers (Q_D), and in the shallow (T_S) and deep (T_D) Tertiary formations located in the Paleogene materials (Fig.1). Most of the locations were sampled during both campaigns.

After measuring groundwater hydraulic head, wells were pumped until the water Eh stabilized. Then, temperature, pH and electrical conductivity (EC) were measured in situ and groundwater samples were collected in bottles that were previously rinsed several

times with groundwater. Samples were stored at 4°C in a dark environment before analysis.

3.2. Analytical techniques

Temperature, pH, EC and Eh were measured using a flow cell to avoid contact with the atmosphere. Aqueous concentrations of chloride, nitrite, nitrate and sulphate were determined by high-performance liquid chromatography (HPLC), HCO₃⁻ aqueous concentration by volumetric titration, and total aqueous concentration of Na, K, Ca, Mg, Fe, Mn and B by inductive-coupled plasma optical emission spectrometry (ICP-OES). Ammonia aqueous concentration was determined by colorimetry (flow injection analysis), and total organic C (TOC) concentration by the organic matter combustion method. All these analyses were done at the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB).

 $δ^2$ H and $δ^{18}$ O of water were measured using the H₂ and CO₂ equilibration techniques respectively. H and O isotope compositions were measured by DI-IRMS on a Delta S Finnigan Mat. $δ^{15}$ N and $δ^{18}$ O of dissolved NO₃⁻ were measured using the AgNO₃ method (modified from Silva et al. (2000)) with an Elemental Analyser (Carlo Erba 1108) coupled with an Isochrom Continuous Flow IRMS in the case of $δ^{15}$ N and with a Thermo-Chemical Elemental Analyser (TC/EA Thermo-Quest Finnigan) coupled with a Delta C Finnigan Mat IRMS in the case of $δ^{18}$ O (duplicate analyses). To measure $δ^{34}$ S and $δ^{18}$ O of SO₄²⁻, aqueous sulphate was precipitated as BaSO₄ by acidifying the sample with HCl, boiling it, and adding an excess of BaCl₂·2H₂O. $δ^{34}$ S was measured using an Elemental Analyser (Carlo Erba 1108) coupled with a Delta C Finnigan Mat, while $δ^{18}$ O was measured with the same methodology (TC/EA-IRMS) as $δ^{18}$ O of nitrate. In order to measure $δ^{11}$ B, sample volume was determined to ultimately yield 6 to 10 µg of B. Samples then underwent a two-step chemical purification using Amberlite IRA-743 selective resin (method adapted from Gaillardet and Allègre (1995)). First, the sample (pH~7) was loaded on a Teflon PFA[®] column filled with a 1 ml resin, previously cleaned with ultrapure water and 2N ultrapure NaOH. After cleaning again the resin with water and NaOH, the purified B was collected with 15 ml of sub-boiled HCl 2N. After neutralisation of the HCl by Superpur NH₄OH (20%), the purified B was loaded again on a small 100 ml resin Teflon PFA[®] column. B was collected with 2 ml of HCl 2N. An aliquot corresponding to 2 mg of B was then evaporated below 70°C with mannitol $(C_6H_8(OH)_6)$ in order to avoid B loss during evaporation (Ishikawa and Nakamura,1990). The dry sample was loaded onto a tantalum (Ta) single filament with graphite (C), mannitol and caesium (Cs). δ^{11} B was determined on the Cs₂BO²⁺ ion (Spivack and Edmond, 1986) by negative-ion Thermal-Ionization Mass Spectrometry (TIMS). The analysis was run in dynamic mode by switching between masses 308 and 309. Each analysis corresponded to 10 blocks of 10 ratios. Samples were always run twice. Total B blank was less than 10 ng corresponding to a maximum contribution of 0.2%, which was negligible. Seawater (IAEA-B1) was purified regularly in the same way, in order to check for a possible chemical fractionation due to an uncompleted recovery of B, and to evaluate the accuracy and reproducibility of the overall procedure. Reproducibility was obtained by repeated measurements of the NBS951 and the accuracy was controlled with the analysis of the IAEA-B1 seawater standard ($\delta^{11}B =$ $38.6\pm1.7\%$). The ¹¹B/¹⁰B ratio of replicate analyses of the NBS951 boric acid standard (after oxygen correction) was 4.05045 ± 0.00130 (2σ , n=183). The reproducibility of the $\delta^{11}B$ was $\pm 0.32\%$ (2 σ). The mean value obtained on $\delta^{11}B$ of seawater was 39.21±0.31‰ (2σ ; n=20). In order to analyse the δ^{13} C of inorganic carbon, water samples were acidified with ortho-phosphoric acid and shaken for at least two hours to convert all bicarbonate into CO₂ and to reach equilibrium between the dissolved and

gaseous phases. Gas samples were then diluted with helium to facilitate the analysis. δ^{13} C was measured on a Gas Chromatograph-Combustion-Isotopic Ratio Mass Spectrometer (GC-C-IRMS). All isotope notations are expressed as δ per mil relative to their respective international standards: Vienna Standard Mean Ocean Water (V-SMOW), atmospheric N₂ (AIR), Vienna Canyon Diablo Troilite (V-CDT), NBS951 and Vienna Pee Dee Belemnite (V-PDB) standards. Reproducibility is ±1.5‰ for δ^{2} H, ±0.2‰ for $\delta^{18}O_{H2O}$, ±0.3‰ for δ^{15} N, ±0.2‰ for δ^{34} S, ±0.5‰ for both $\delta^{18}O_{NO3}$ and $\delta^{18}O_{SO4}$, ±0.3‰ for δ^{11} B, and ±0.3‰ for $\delta^{13}C_{HCO3}$.

For isotope analyses, samples were prepared at the laboratory of the Mineralogia Aplicada i Geoquimica de Fluids research group of the Universitat de Barcelona and the analyses were performed at the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiT-UB), except those of δ^{11} B that were analysed at the BRGM (France) and those of δ^{13} C that were analysed at the Environmental Isotope Laboratory (EIL) of the University of Waterloo (Canada).

4. Results and discussion

Groundwater hydraulic head, hydrochemical and isotope data of the two campaigns are reported in Tables 1, 2 and 3.

4.1. Hydrodynamic data and potentiometric map

Hydraulic head measurements in the Quaternary aquifer conducted during the August campaign were used to draw the potentiometric contour lines shown in Fig.1, as this represents the largest pressure in the groundwater system resources. The generated potentiometric map shows that groundwater flow lines were mainly oriented along a south to north trend (from the Gavarres massif to the Ter River) (Fig. 1) although close to the Ter River, groundwater flow changed to a west-to-east direction towards the sea. The potentiometric map also reflects the depression cone of the Gualta village resulting from the intense groundwater withdrawal activity of its supply wells. However, it was not possible to draw a consistent potentiometric plot of the Tertiary aquifer able to corroborate the upward vertical flow line connecting the underlying confined fractured Tertiary unit to the shallow Quaternary aquifer that was suggested by Vilanova et al. (2008). Potentiometric levels in the Tertiary aquifer may vary seasonally due to groundwater pumping, controlling the recharge relation with the Ter River alluvial aquifer.

4.2. δ^2 H and δ^{18} O data. Sources of recharge

Fig. 2 shows that δ^2 H and δ^{18} O of groundwater samples from both campaigns mostly plot under the annual Local Meteoric Water Line LMWL (Vilanova et al., 2008).

However, the wide range of δ^2 H and δ^{18} O values from the Quaternary aquifer indicates the implication of several recharge flow systems affecting the aquifer. Some of the samples fall very close to the weighted mean precipitation (δ^2 H = -33.5‰, δ^{18} O = -5.2‰) calculated from the Mas Badia station data (located in the Baix Ter basin; Fig. 2) showing the influence of the infiltration of rainfall into the basin. Samples located at the NW of the shallow Quaternary aquifer (Q₇, Q₈ and Q₁₂) yielded lighter isotope compositions with values similar to those of the Ter River reported by Vilanova (2004; δ^2 H from -50 to -45‰, δ^{18} O from -8 to -7‰), indicating a contribution from the Ter River to the alluvial aquifer groundwater. Finally, other samples from the Quaternary aquifer present δ^2 H and δ^{18} O compositions intermediate between those influenced by the rainfall and those influenced by the Ter river water (Fig. 2) but also close to those of sample T₂₁, located in the Gavarres massif foothill (south of the study area, Fig. 1). Thus, these samples can be geochemically and isotopically considered as representative of the recharge from the Gavarres massif, given its very low mineralization and its isotope composition (Fig.2). As irrigation demand is fully covered by groundwater in

the sampled area, the potential effects of irrigation returns on groundwater isotopic composition would not in any case modify the recharge model herein proposed.

In Tertiary aquifers, most of the groundwater samples fell between the weighted mean precipitation signature and the isotope composition of groundwater from the Gavarres massif (Fig. 2). They present a narrower range of δ^2 H and δ^{18} O compositions, although they overlap with the intermediate isotopic composition of the Quaternary aquifer groundwater samples (Fig. 2). This overlap suggests that both aquifers share a common source of recharge or are somehow connected. This is consistent with the conceptual model described by Vilanova et al. (2008) in which an upward groundwater flow was proposed connecting the Tertiary aquifer to the deep Quaternary aquifer in the northern part of the area. Therefore, the contribution from the Tertiary units towards the Quaternary aquifer cannot be discarded despite the fact that this could not be supported by the potentiometric map.

4.3. Hydrochemical data

Chemical data for groundwater samples collected in the Baix Ter basin (Tables 1 and 2) showed a HCO₃⁻-Ca²⁺-Mg²⁺ facies, in accordance with the hydrochemistry being controlled by carbonate dissolution reactions that occur throughout the Tertiary materials and alluvial formations. The rapid kinetic of carbonate dissolution hides the hydrochemical characteristics acquired from the igneous and metamorphic rocks of the Gavarres massif (Vilanova et al., 2008). Groundwater pH values were all above 7.4, HCO₃⁻ concentrations were between 177 and 619 mg L⁻¹ and EC varied from 552 μ S cm⁻¹ to 2993 μ S cm⁻¹.

In all the studied area, NO_3^- concentrations presented a wide range of values from below the detection limit (0.1 mg L⁻¹) to concentrations up to 480 mg L⁻¹. 60% of the studied samples had NO_3^- levels above the legal threshold of 50 mg L⁻¹ for drinking

water (EC, 1998). No NO₂⁻ was detected. Ammonium concentration ranged between 0.08 mg L^{-1} and 0.47 mg L^{-1} . It can be observed that NO₃⁻ concentrations of the river samples presented values of 9 and 7 mg L⁻¹, consistent with surface water nitrate values and lower than the monthly NO₃⁻ average for the Ter River (15 mg L⁻¹; σ = 5.1, n = 37) between 2003 and 2006 (ACA, 2015). However, nitrate concentration in aquifers showed a diffuse spatial distribution. In shallow aquifers (Q_S and T_S), nitrate concentrations ranged from 6 to 480 mg L^{-1} , while in deeper aquifers they went from values below detection limit up to 265 mg L^{-1} . This distribution does not seem to be linked to any specific groundwater flow direction nor limit of the aquifer units. It can be explained by the highly complex hydrogeology of the study zone and its distinct recharge areas, and by the mixing of waters from distinct origins and qualities within the well borehole. Several factors such as the intended exploitation of different levels to increase the well efficiency, the possible lack of well casing derived from an incomplete borehole construction, and/or the presence of preferential flow paths through fractures or fault zones that connect local and regional flow systems, i.e. Quaternary and Tertiary aquifers could account for the mixing of waters. Moreover, the intensive pumping during irrigation and low rainfall periods can also enhance re-circulation between aquifer levels, mainly from the shallow to deeper ones, resulting in a decrease of the quality of the water resources stored in the deeper aquifer layers.

The lowest NO_3^- contents in the Quaternary aquifer were observed near the Ter River suggesting some influence from induced stream recharge; and in the SE area, near the Gavarres Range, in the Tertiary aquifer.

During the first sampling campaign, two samples from the shallow Quaternary aquifer (Q_4 and Q_8 , Table 2) presented NO_3^- concentrations of 6 mg L⁻¹ and 13 mg L⁻¹, respectively, coupled with high levels of Mn (4.4 and 0.8 mg Mn L⁻¹) and around 2 mg

 L^{-1} of total organic carbon. Two samples in the Q_D (Q_1 and Q_2) and three samples in T_D aquifers (T_9 , T_{10} and T_{14}) had NO₃⁻ below detection limit, an Eh value below 200 mV and showed the highest ammonium and manganese concentrations (Tables 1 and 2, Fig.3). Moreover, NO₃⁻ in Q_2 has been monitored through time and has always been below detection limit. These characteristics are typical of groundwater under reducing conditions, and would suggest that they are undergoing denitrification processes. However, measured TOC concentrations for Q_1 , Q_2 , T_9 , T_{10} and T_{14} (between 0.4 and 1.2 mg L^{-1}) are not high enough to stoichiometrically allow the reduction of NO₃⁻ by oxidation of organic matter in anaerobic conditions (Rivett et al., 2008), but they may indicate the presence of organic matter that could represent a residual content after previous consumption by heterotrophic denitrifying bacteria.

Some samples with high NO₃⁻ concentration (Q₅, Q₁₀, Q₁₅ and Q₁₆ from Q₈, T₁₇ and T₂₀ from T_s, and T₃, T₅ and T₈ from T_D) also presented high sulphate and chloride concentrations (up to 371 and 362 mg L⁻¹, respectively) (Fig. 4a, b). Considering that CI⁻ is a conservative element largely unaffected by physical, chemical and microbiological processes occurring in the groundwater (Altman and Parizek, 1995), the [NO₃⁻]/[CI⁻] ratio can be used to eliminate the potential effect of dilution. In Fig. 4c, sulphate concentration is plotted against the [NO₃⁻]/[CI⁻] ratio. Groundwater SO₄²⁻ varied between 29 and 371 mg L⁻¹, with an average value of 108 mg L⁻¹ (n = 64). But a set of samples, with 1<[NO₃⁻]/[CI⁻]<2, present moderate SO₄²⁻ concentrations but also high NO₃⁻ and consequently high CI⁻ concentrations. Samples with [NO₃⁻]/[CI⁻]>2 had high NO₃⁻ but lower SO₄²⁻ concentrations (Fig. 4c).

Since no evaporitic or gypsum outcrops nor disseminated pyrite exist in the study area, these SO_4^{2-} concentrations must originate from anthropogenic sources such as manure, synthetic fertilizers or sewage. High Cl⁻ concentrations can be caused by the

input of organic fertilizers since they generally show elevated chloride concentrations (Karr et al., 2001; Menció et al. 2016). All these observations suggest that both the mineral and the organic fertilizers are the major vectors of contamination.

In most of samples, B concentration was below the detection limit. However, B concentrations around 0.1-0.2 mg L⁻¹ have been measured in samples with high nitrate, sulphate and chloride concentrations (e.g. Q10 and Q15, Fig. 4d) suggesting sewage and manure as other potential contamination sources. However, as seen in Fig. 4d, samples with the highest B concentration (up to 232 μ g/L) presented intermediate nitrate concentrations (25-45 mg NO₃⁻ L⁻¹), showing that the presence of B in groundwater is not necessarily linked to high NO₃⁻ concentrations.

Thus, our results show that groundwater is probably affected by more than one source of contamination and that natural denitrification may be acting in some areas. However, the unambiguous identification of these sources and processes based on the sole hydrochemical data is somewhat difficult as the signal may be hindered by the mixing of groundwaters from different layers and recharge flow systems.

4.4. Isotope data. Pollution sources and attenuation processes

4.4.1. δ^{15} N and δ^{18} O of NO₃⁻

NO₃⁻ isotope composition in groundwater ranged between +5.0 and +32.5‰ for δ^{15} N, with an average value of +13.0‰ (n = 58), and between +1.8 and +18.1‰ for δ^{18} O, with an average value of +7.1‰ (n = 58) (Table 3).

As seen in Fig. 5a, five groundwater samples (Q_{14} and Q_{16} from Q_8 , T_3 from T_D , and T_{18} and T_{21} from T_8) presented $\delta^{15}N$ values compatible with soil organic nitrogen (from +3 to +8‰), fertilizers (-4 to +8‰) and sewage (+5 to +20‰) (Table 4). Within these samples, only sample T_{21} presented low nitrate, sulphate and chloride concentration (6 mg L⁻¹ NO₃⁻, 36 mg L⁻¹ Cl⁻ and 30 mg L⁻¹ SO₄²⁻). The low $\delta^{15}N$ (+5.0‰) measured in sample T_{21} , coupled with its $\delta^2 H$ and $\delta^{18}O$, that are similar to those of the Gavarres massif (Fig. 2), indicate that the NO₃⁻ for these samples is consistent with a natural soil origin. T_{21} represents thus the local NO₃⁻ background. However, as for samples Q₁₄, Q₁₆, T₃, and T₁₈, nitrate contents range from 65 to 222 mg L⁻¹. The origin of NO₃⁻ for these samples cannot be solely attributed to the mineralization of soil nitrogen (as in T₂₁) which cannot explain such high concentrations.

Therefore, although a small contribution of soil organic nitrogen is possible (Wassenaar, 1995) measured isotope values may originate from synthetic fertilizers or sewage/manure sources or from a mixing of both (Fig. 5a).

Most of the samples presented δ^{15} N ranging between +8 and +16‰, indicating that NO₃⁻ may originate from ¹⁵N-enriched anthropogenic organic matter (manure or sewage) (Fig. 5a). Finally, some samples (Q₄, Q₈ and Q₉, from Q_S, and T₂ from T_D) presented δ^{15} N values higher than +16‰, coupled to low NO₃⁻ contents (between 6 and 26 mg L⁻¹, Table 2) and high $\delta^{18}O_{NO3}$ values (close to +10‰). The range of $\delta^{18}O$ of NO₃⁻ for NH₄⁺ fertilizers, soil nitrogen and manure and sewage provided in Table 4 and plotted in Fig. 5a (+3.4‰ to +4.6‰), has been estimated according to eq. 5 (Anderson and Hooper, 1983; Hollocher, 1984; Kendall et al., 2007), where the $\delta^{18}O_{H2O}$ values are the highest and lowest groundwater $\delta^{18}O$ measured in the Baix Ter basin, and the $\delta^{18}O_{O2}$ is that of the atmospheric O₂ (+23.5‰; Horibe et al., 1973).

$$\delta^{18}O_{NO3} = 2/3(\delta^{18}O_{H2O}) + 1/3(\delta^{18}O_{O2})$$
(5)

 $\delta^{18}O_{NO3}$ values measured in the groundwater samples ranged from +1.8‰ to +18.1‰ (Fig.5b). While nitrate fertilizers are currently applied onto local crops their direct contribution to groundwater nitrate must be discarded as $\delta^{18}O$ and $\delta^{15}N$ of groundwater NO₃⁻ fall very far from nitrate fertilizers values (Fig. 5a). Moreover, most

of samples had $\delta^{18}O_{NO3}$ higher than the calculated values for full equilibrium with the $\delta^{18}O$ of groundwater. Both results could be interpreted as a consequence of three different processes: i) the mineralization-immobilization-turnover (MIT) process, ii) the higher consumption of NO₃⁻ from mineral fertilizers compared to that of ammonium in the root zone and iii) the reduction of NO₃⁻ via denitrifying bacteria. The MIT process consists of a microbial-mediated immobilization of nitrate N as organic nitrogen, the subsequent mineralization of this organic nitrogen to ammonium, and finally the nitrification of this ammonium back to NO₃⁻ (Mengis et al., 2001). This turnover process results in an important ¹⁸O depletion of the initial $\delta^{18}O_{NO3}$ of the synthetic fertilizers (+17‰ to +20‰, Table 4). As synthetic fertilizers are currently used in the area, MIT process must be very active in order to explain why our results do not show the low $\delta^{15}N$ and high $\delta^{18}O$ values of nitrate from synthetic fertilizers. This indicates all NO₃⁻ from synthetic fertilizers that infiltrated underwent this process and that this source cannot be dismissed.

As pig manure is mainly liquid, the infiltration of ammonium from manure through the non-saturated zone to the saturated one is faster than that of nitrate from solid synthetic fertilizers, which need to be dissolved by rain or irrigation. Ammonium soil sorption capacity can be considered negligible as the soil is already saturated due to the long-standing fertilization practices affecting the area. Ammonium is also fast and completely nitrified into nitrate in the non-saturated zone. All these elements favour ammonium from pig manure to reach the saturated zone polluting groundwater. On the contrary, nitrate from synthetic fertilizers remains on the agricultural soil, incorporated and stored in the soil organic matter pool by means of the MIT process. It could then be slowly rereleased for either uptake by crops or export into the hydrosphere (Sebilo et al., 2013). Finally, the reduction of NO_3^- via denitrifying bacteria, which is characterized by

a heavy-isotope enrichment of both the δ^{15} N and δ^{18} O of the residual nitrate, can overprint the mixing of potential end-members and can significantly alter both the NO₃⁻ concentration (i.e. attenuation) and corresponding N and O isotope compositions. δ^{15} N and δ^{18} O of NO₃ from the Ter River samples were in agreement with a wastewater origin.

Ten of the samples had $\delta^{18}O_{NO3}$ and $\delta^{15}N$ higher than +8‰ and +15‰, respectively. Fig. 5a shows that these samples roughly aligned following a $\varepsilon_N:\varepsilon_O$ ratio of 2, consistent with natural denitrification (Kendall et al., 2007). This means that the nitrate isotopic compositions but also the low nitrate concentration measured in those samples result from natural denitrification processes occurring in the aquifers. This is confirmed by Fig. 5b, in which a negative linear correlation between $\delta^{18}O_{NO3}$ and $\ln(NO_3^-/C\Gamma)$ is observed for these samples, indicating that denitrification is taking place (Vitòria et al. 2008). The highest denitrified samples (i.e. with the higher coupled $\delta^{18}O_{NO3}$ and $\delta^{15}N$) were observed either in the shallow Quaternary levels near the Ter River (Q₄, Q₈, Q₉) or in the Tertiary aquifers (T₂). Moreover, the NO₃⁻ concentration measured below the detection limit in the samples Q₁, Q₂, T₉, T₁₀ and T₁₄ (Fig. 2) can also be interpreted as resulting of natural denitrification. Considering that no significant variations were identified in both the isotope and chemical compositions of our samples between both campaigns, it can be inferred that natural denitrification had a moderate activity and/or that NO₃⁻ attenuation was balanced by the input of new NO₃⁻ into the aquifer.

4.4.2. δ^{34} S and δ^{18} O of SO₄

 SO_4^{2-} isotope compositions ranged between -16.0 and +14.7‰ for $\delta^{34}S$, with an average value of +4.5‰ (n = 64), and between +3.8 and +16.1‰ for $\delta^{18}O_{SO4}$, with an average value of +7.2‰ (n = 64) (Table 3, Fig. 6). Most of the groundwater samples fall within the area defined by the isotope signatures of local anthropogenic sources (Table

4) showing that SO_4^{2-} in the Baix Ter groundwater can be explained by a ternary mixing between: 1) mineral fertilizers, 2) sewage and 3) pig manure (Fig. 6). This comforts the conclusions from the study of sulphate and nitrate groundwater concentrations.

Still, the δ^{34} S and a $\delta^{18}O_{SO4}$ values measured between 0 and +6‰ of samples Q₁₇, T₁₁, T₁₈ and T₂₁ could indicate a soil origin (Table 4), in agreement with their low SO₄²⁻ concentrations (around 30 mg SO₄²⁻ L⁻¹).

Two sampling sites (T₂ and T₁₄) yielded the lowest negative δ^{34} S values and had $\delta^{18}O_{SO4}$ around +5‰, revealing a SO₄²⁻ contribution from a ³⁴S-depleted source of reduced S (Fig. 6). Moreover, both T₂ and T₁₄ showed very low (9 mg L⁻¹) or below detection limit (0.1 mg L⁻¹) nitrate concentrations, respectively. On the contrary, samples Q₁, Q₂, T₉ and T₁₀, with nitrate concentration below the detection limit (0.1 mg L⁻¹) exhibited the highest δ^{34} S and $\delta^{18}O_{SO4}$ values (+14.7‰ and +16.1‰ respectively).

All these samples in which nitrate concentration is below detection limit, together with other samples with very low nitrate aqueous concentration (NO₃⁻ < 25 mg L⁻¹) and $\delta^{18}O_{SO4}$ higher than +8‰ define a linear trend with $\varepsilon_S/\varepsilon_O = 1/0.31=3.2$ compatible with a bacteriogenic reduction of SO₄²⁻ (Mizutani and Rafter, 1973) (Fig. 6). This is consistent with their corresponding low Eh values and high Mn concentrations (Fig. 3). However, as the presence of pyrite and gypsum in the area is scarce, autotrophic denitrification can be discarded as the main denitrifying process occurring in the study zone.

 δ^{34} S and $\delta^{18}O_{SO4}$ of the Ter River samples also indicated, in agreement with their δ^{15} N and $\delta^{18}O_{NO3}$ that the dissolved SO₄²⁻ in surface waters originated from wastewater. **4.4.3.** δ^{11} B Boron isotopes measurements were performed in 12 groundwater samples, selected considering both their NO_3^- and B contents and their location in the vicinity of pig farms or urban areas with the aim of discriminating between these two origins.

Pig manure present δ^{11} B values ranging from +19.5‰ to +42.4‰, significantly higher than urban wastewater values that range from -7.7‰ to +12.9‰ (Table 4). However, mineral fertilizers are characterized by a δ^{11} B range similar to sewage (-9‰ to +15‰, Table 4). Although mineral fertilizers can present a wide range of B concentrations they usually have lower B contents compared pig manure (Fig. 7a).

 δ^{11} B composition of dissolved B in selected groundwater samples ranged between +1.4‰ and +34.5‰, with an average value of +24.1‰ (n = 12). B concentrations in these samples ranged between 0.055 and 0.232 mg L⁻¹. No trends or enrichment in δ^{11} B composition of dissolved B with decreasing B content were observed (Fig. 7a), indicating that B is not explained by binary mixing relationships and that no significant sorption/desorption processes of B onto/from clay minerals are occurring. Most samples fell in the isotope range of pig manure (Fig. 7a and 7b). This is in agreement with the conclusions drawn from the NO₃⁻ and SO₄²⁻ isotope data. Two of the samples showed δ^{11} B values consistent with a wastewater origin. They correspond to groundwater collected in La Bisbal (Q₂₀) and Ullastret (Q₂₁) water supply wells (Fig. 1), located downstream the discharge of the La Bisbal water treatment plant into the Daró River.

Boron analyses, thus, suggest that pig manure is the main source of contamination and that the influence of sewage and mineral fertilizers is lower than the contribution from organic residues.

4.4.4. δ^{13} C of HCO₃⁻

Samples presented $\delta^{13}C_{HCO3}$ values between -6.5‰ and -16.2‰ (Table 3). $\delta^{13}C_{HCO3}$ values of marine marls in the study zone are $\delta^{13}C \sim 0$ ‰. Typical $\delta^{13}C$ values for CO₂

dissolved in the soil are between -14‰ and -16‰; for soil HCO₃⁻ δ^{13} C values are around -23‰ and for pig manure, mineral fertilizers and sewage, δ^{13} C values range from -23.8‰ to -16.4‰, from -35‰ to -24‰ and from -25‰ to -13‰, respectively (Table 4).

Denitrification catalysed by organic matter oxidation induces a decrease in NO₃⁻ and in total organic carbon concentrations coupled with an increase in dissolved inorganic carbon concentration (eq.1), causing an increase of δ^{15} N and $\delta^{18}O_{NO3}$ and a decrease in $\delta^{13}C_{HCO3}$ (Faure, 1977).

Fig. 8a shows the evolution of the $\delta^{18}O_{NO3}$ as a function of ln(NO₃⁻/HCO₃⁻). A slight increase in $\delta^{18}O_{NO3}$ coupled to a decrease in ln(NO₃⁻/HCO₃⁻) can be observed that would suggest that denitrification may occur. Nevertheless, we were not able to observe the corresponding decrease in $\delta^{13}C_{HCO3}$ in our results (Fig. 8b). As already discussed porewaters presented HCO₃⁻-Ca²⁺-Mg²⁺ facies, with saturation indices for Ca-Mgcarbonates between -1 and 1. This indicates that bicarbonate is in equilibrium with Ca-Mg-carbonates whose dissolution and precipitation will contribute to the buffering of the $\delta^{13}C_{HCO3}$ of our samples with a final isotope composition corresponding to sedimentary rocks ($\delta^{13}C$ around 0 ‰ after Travé et al., 1997). Besides these dissolution/precipitation reactions, $\delta^{13}C_{HCO3}$ can be also affected by other reactions such as equilibrium with CO₂(g) and other sources such as manure or sewage (Clark and Fritz, 1997).

5. Conclusions

Here we have coupled the study of hydrochemical and multi-isotope data with hydrogeological framework information to identify the sources and to characterise processes controlling the budget of dissolved NO_3^- in ground- and surface water in a complex hydrogeological system (the Baix Ter basin).

Isotope data have shown that the sources of recharge for both the Tertiary and the Quaternary aquifers are the rainfall, the Ter River in the NW and a contribution from Les Gavarres Massif. Moreover, they showed that dissolved NO₃⁻ in groundwater in the study area mainly comes from pig manure application onto the fields, with minor contributions from sewage and mineral fertilizers. The study of δ^{11} B confirmed pig manure as the main vector of pollution but also identified an urban origin for two of the analysed wells. The dual-isotope (δ^{15} N and δ^{18} O of NO₃) approach indicated that mineralization-immobilization-turnover (MIT) and natural denitrification processes are occurring within the study area. The δ^{34} S and δ^{18} O of SO₄²⁻ showed that NO₃⁻ reduction is not controlled by the oxidation of pyrites but rather by the oxidation of organic matter. However, the role of organic matter in NO₃⁻ attenuation could neither be confirmed nor discarded by the study of the $\delta^{13}C_{HCO3}$ as other processes and sources ultimately buffered these isotope compositions. The consumption of organic matter in anaerobic environments is favoured by 1) the river-aquifer connection, 2) the existence of some organic layers in the Ter riversides, and 3) mixing between polluted groundwater and deep regional flows with reducing conditions.

Since the role of organic matter in the NO₃⁻ reduction is still an on-going research, further studies on the δ^{13} C of local contaminant sources and on the role of MnO₂ should be further investigated. Even if working with samples from exploitation wells, it has been proved that multi-isotope studies allow us to: i) describe groundwater dynamics, ii) discriminate between sources of pollution and determine their relative contribution, iii) characterise the processes affecting the overall nitrogen budget, such as natural attenuation, that in another way would go unnoticed. Still, these approaches highly depend on the knowledge of the isotopic signatures of the different potential sources of nitrate contamination of a given area, on the complexity of the aquifers complex and on the availability of a good infrastructure (e.g. multi-piezometers).

Acknowledgements

This research was funded by the ATENUATION (CGL2011-29975-C04-01) and REMEDIATION (CGL2014-57215-C4-1-R) projects from Spanish Ministry of Economy and Competitiveness (MINECO) and the AGAUR from the Catalan Government (grant 2014SGR-1456). We would like to thank the Centres Científics i Tecnològics of the Universitat de Barcelona for its laboratory help. Authors acknowledge the fruitful comments of the three anonymous reviewers.

References

- ACA, 2007. Diagnosis de la causalidad de la contaminación por nitratos de algunos abastecimientos públicos en las zonas vulnerables de Cataluña, análisis de alternativas, medidas de prevención y corrección. Área vulnerable 1 Girona. Estudio 1: Llanura aluvial de los ríos Ter y Daró, provincia de Girona. ACA (Water Catalan Agency) Internal Report. 168 pp.
- ACA, 2015. Agència Catalana de l'Aigua. Generalitat de Catalunya. Consulta de dades. Available at: http://aca-web.gencat.cat/aca/appmanager/aca/aca/ (June 2016).
- Altman, S.J., Parizek, R.R. 1995. Dilution of non-point source nitrate in ground water.J. Environ. Qual. 24, 707-718.
- Amiri, H., Zare, M., Widory. D., 2015. Assessing sources of nitrate contamination in the Shiraz urban aquifer (Iran) using the δ^{15} N and δ^{18} O dual-isotope approach. Isotopes in Environmental and Health Studies. DOI: 10.1080/10256016.2015.1032960.
- Anderson, K. K., Hooper, A. B., 1983. O₂ and H₂O are each the source of one O in NO₂⁻ produced from NH₃ by Nitrosomas-¹⁵N-NMR evidence. FEBS Letters, 64, 236–40.
- Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic tanks. Ground Water, 31, 180–186.
- Aravena, R., Robertson, W.D., 1998. Use of Multiple Isotope Tracers to Evaluate Denitrification in Ground Water: Study of Nitrate from a Large-Flux Septic System Plume. Ground Water, 36, 975-982.
- Aravena, R., Mayer, B., 2010. Isotopes and Processes in the Nitrogen and Sulfur Cycles. In: Aelion, C.M., Höhener, P., Hunkeler, D., Aravena, R. (Eds.),

Environmental Isotopes in Biodegradation and Bioremediation. CRC Press, pp. 203–246.

- Barroso, M.F., Ramalhosa, M.J., Olhero, A., Antão, M.C., Pina, M.F., Guimarães, L.,
 Teixeira, J., Alfonso, M.J., Delerue-Matos, C., Chaminé, H.I., 2015. Assessment
 of groundwater contamination in an aricultural peri-urban area (NW Portugal):
 an integrated approach. Environ Earth Sci 73, 2881-2894.
- Basset, R.L., Buszka, P.M., Davidson, G.R., Chong-Diaz, D., 1995. Identification of groundwater solute sources using boron isotopic composition. Environ. Sci. Technol. 29, 2915–2922.
- Borch, T., Kretzschmar, R., Kappler, A., Van Cappellen, P., Ginder-Vogel, M., Voegelin, A., Campbell, K., 2010. Biogeochemical Redox Processes and their Impact on Contaminant Dynamics. Environmental Science and Technology, 44, 15–23.
- Böttcher, J., Strebel, O., Voerkelius, S., Schmidt, H.L., 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in sandy aquifer. Journal of Hydrology, 114, 413-424.
- Bryan, N.S., Alexander, D.D., Coughlin, J.R., Milkowski, A.L., Boffetta, P., 2012. Ingested nitrate and nitrite and stomach cancer risk: An updated review. Food and Chemical Toxicology, 50, 3646–3665.
- Clark, I.D., Fritz, P., 1997. Environmental Isotopes in Hydrogeology. Lewis Publishers, New York. 352 pp.
- Cravotta, C.A., 1997. Use of Stable Isotopes of Carbon, Nitrogen and Sulphur to Identify Sources of Nitrogen in Surface Waters in the Lower Susquehanna River Basin, Pennsylvania. U.S. Geological Survey Water-Supply Paper 2497.

- Curt, M.D., Aguado, P., Sánchez, G., Bigeriego, M., Fernández, J., 2004. Nitrogen isotope ratios of synthetic and organic sources of nitrate water contamination in Spain. Water, Air and Soil Pollution, 151, 135-142.
- Delconte. C.A., Sacchi, E., Racchetti, E., Bartoli, M., Mas-Pla, J., Re, V., 2014.
 Nitrogen inputs to a river course in a heavily impacted watershed: a combined hydrochemical and isotopic evaluation (Oglio River Basin, N Italy). Science of the Total Environment 466-467, 924-938, DOI: 10.1016/j.scitotenv.2013.07.092.
- EC (European Communities), 1991. Council Directive 91/676/EC, of 12 December 1991, concerning the protection of waters against pollution caused by nitrates from agricultural sources.
- EC (European Communities), 1998. Council Directive 98/83/EC, of 3 November 1998, on the quality of water intended for human consumption.
- EC (European Communities), 2000. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy (Water Framework Directive). Official Journal of the European Communities, OJ L 327.
- EC (European Communities), 2006. Directive 2006/118/EC of the European Parliament and of the Council on the protection of groundwater against pollution and deterioration (Groundwater Directive). Official Journal of the European Communities, OJ L 372.
- EEA (European Environment Agency), 1999. Nutrients in European Ecosystems. Environmental assessment report Nº 4.
- EEA (European Environment Agency), 2012. European waters: assessment of status and pressures. EEA Report Nº 8. Published: Nov 13, 2012. Copenhagen, Denmark.

EEA (European Environment Agency), 2015. Nutrients in freshwater. Indicator assessment. Data and maps. IND-8-en. CSI 020, WAT 003. Published: Sep 4th, 2015. Copenhagen, Denmark. Available as a website at <u>http://www.eea.europa.eu/data-and-maps/indicators/nutrients-</u> infreshwater/nutrients-in-freshwater-assessment-published-6.

Faure, G. 1997. Principles of isotope geology, Wiley, 2nd Ed, 589 pp.

- Fukada, T., Hiscock, K., Dennis, P.F., Grischek, T., 2003. A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site. Water Res. 37, 3070–3078.
- Gaillardet, J., Allègre, C.J., 1995. Boron isotopic compositions of corals: Seawater or diagenesis record? Earth and Planetary Science Letters 136, 665-676.
- Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chem. Geol. 59, 87–102.
- Hollocher, T. C., 1984. Source of oxygen atoms in nitrate in the oxidation of nitrite by *Nitrobacter agilis* and evidence against a P-O-N anhydride mechanism in oxidative phosphorylation. Archives of Biochemistry and Biophysics, 233, 721–27.
- Horibe, Y., Shigehara, K., Takakuwa, Y., 1973. Isotope separation factors of carbon dioxide-water system and isotopic composition of atmospheric oxygen. Journal of Geophysical Research, 78, 2625-2629.
- Ishikawa, T., Nakamura, E., 1990. Suppression of boron volatilization from a hydrofluoric acid solution using a boron-mannitol complex. Analytical Chemistry 62, 2612–2616.

- Jurado, A., Vàzquez-Suñé, E., Soler, A., Tubau, I., Carrera, J., Pujades, E., Anson, I., 2013. Application of multi-isotope data (O, D, C and S) to quantify redox processes in urban groundwater. Applied Geochemistry, 34, 114–125.
- Karr, J.D., Showers, W.J., Wendell Gilliam, J., Scott Andres, A., 2001. Tracing nitrate transport and environmental impact from intensive swine farming using delta nitrogen-15. J. Environ. Qual. 30, 1163–1175.
- Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Tracing anthropogenic inputs of nitrogen to ecosystems, Chapter 12. In: R.H. Michener and K. Lajtha (Eds.), Stable Isotopes in Ecology and Environmental Science, 2nd edition, Blackwell Publishing, pp. 375-449.
- Koba, K., Tokuchi, N., Wada, E., Nakajima, T., Iwatsubo, G., 1997. Intermittent denitrification: the application of a ¹⁵N natural abundance method to a forested ecosystem. Geochim. Cosmochim. Acta, 61, 5043–5050.
- Komor, S.C., 1997. Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota. J. Environ. Qual. 26, 1212–1222.
- Krouse, H.R., Mayer, B., 2000. Sulphur and oxygen isotopes in sulphate. In: Cook,P.G., Hercseg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology.Kluwer Academic Press, Boston, pp. 195–231.
- Li, X.D., Liu, C.Q., Harue, M., Li, S.L., Liu, X.L., 2010. The use of environmental isotopic (C, Sr, S) and hydrochemical tracers to characterize anthropogenic effects on karst groundwater quality: A case study of the Shuicheng Basin, SW China. Applied Geochemistry, 25, 1924–1936.
- Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, P., 1981. Experimental determination of nitrogen kinetic isotope fractionation: some

principles, illustration for the denitrification and nitrification processes. Plant Soil, 62, 413–430.

- Mariotti, A., Landreau, A., Simon, B., 1988. ¹⁵N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. Geochim. Cosmochim. Acta, 52, 1869–1878.
- Mas-Pla, J., Bach, J., Montaner J., 1998. Distribución de la concentración de nitratos en el sistema hidrogeológico Baix Ter-Gavarres (Girona). In: La contaminación de las aguas subterráneas: Un problema pendiente. ITGE-AIH, pp. 139–145.
- Mas-Pla, J., Vilanova, E., 2001. Dinámica del sistema hidrogeológico Baix Ter-Gavarres en base a isótopos estables. In: IGME, Las Caras del Agua, Serie Hidrogeología y Aguas Subterráneas n. 1/2001, tomo I, pp. 395-402.
- Menció, A., J. Mas-Pla, A. Soler, N. Otero, O. Regàs, M. Boy-Roura, R. Puig, J. Bach,
 C. Domènech, A. Folch, M. Zamorano, D. Brusi (2016). Nitrate pollution of
 groundwater; all right ..., but nothing else? Science of the Total Environment,
 539C: 241-251. DOI: 10.1016/j.scitotenv.2015.08.151
- Mengis, M., Walther, U., Bernasconi, S.M., Wehrli, B., 2001. Limitations of using δ¹⁸O for the source identification of nitrate in agricultural soils. Environ. Sci. Technol. 35 (9), 1840–1844.
- Michalski, G., Kolanowski, M. Rihaa, K.M., 2015. Oxygen and nitrogen isotopic composition of nitrate in commercial fertilizers, nitric acid, and reagent salts.Isotopes in Environmental and Health Studies 51, 382-391.
- Mizutani, Y., Rafter, T.A., 1973. Isotopic behaviour of sulphate oxygen in the bacterial reduction of sulphate. Geochemical Journal, 6, 183-191.
- Montaner, J., Pons, P., López, J., 2010. Caracterització del flux hidrològic a la plana litoral del Baix Ter. In: El flux hidrològic de la plana litoral del Baix Ter.

Evolució fluvial, caracterització hidrològica i pautes de gestió. Montaner, J. (coord.). Càtedra d'Ecosistemes Litorals Mediterranis. Museu de la Mediterrània (Ed.). Recerca i Territori, 2.

- Neal, C., Neal, M., Warrington, A., Àvila, A., Piñol, J., Rodà, F., 1992. Stable hydrogen and oxygen isotope studies of rainfall and streamwaters for two contrasting holm oak areas of Catalonia, northeastern Spain. Journal of Hydrology, 140, 163–178.
- Otero, N., Canals, A., Soler, A., 2007. Using dual-isotope data to trace the origin and processes of dissolved sulphate: a case study in Calders stream (Llobregat basin, Spain). Aquat. Geochem. 13, 109–126.
- Otero, N., Soler, A., Canals, A., 2008. Controls of δ³⁴S and δ¹⁸O in dissolved sulphate: Learning from a detailed survey in the Llobregat River (Spain). Applied Geochemistry, 23, 1166-1185.
- Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J., 2009. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: the case of Plana de Vic (Osona, Spain). Agr. Ecosyst. Environ. 133 (1-2), 103–113.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. Chemical Geology, 179, 113-128.
- Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Res. 42, 4215–4232.
- Rock, L., Mayer, B., 2002. Isotopic assessment of sources and processes affecting sulphate and nitrate in surface water and groundwater of Luxembourg. Isotopes Environ. Health Stud. 38 (4), 191-206.

- Sacchi, E., Acutis, M., Bartoli, M., Brenna, S., Delconte. C.A., Laini, A., Pennisi, M.(2013) Origin and fate of nitrates in groundwater from the central Po plain: Insights from isotopic investigations. Applied Geochemistry 34, 164-180.
- Saccon, P., Leis, A., Marca, A., Kaiser, J., Campisi, L., Böttcher, M.E., Savarino, J., Escher, P., Eisenhauer, A., Erbland, J., 2013. Multi-isotope approach for the identification and characterization of nitrate pollution sources in the Marano lagoon (Italy) and parts of its catchment area. Appl. Geochem., 34, 75–89.
- Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., Mariotti, A., 2013. Long-term fate of nitrate fertilizer in agricultural soils. PNAS (Proceedings of the National Academy of Sciences of the United States of America). www.pnas.org/cgi/doi/10.1073/pnas.1305372110
- Seiler, R. L., 2005. Combined use of ¹⁵N and ¹⁸O of nitrate and ¹¹B to evaluate nitrate contamination in groundwater. Applied Geochemistry, 20, 1626-1636.
- Silva, S.R., Ging, P.B., Lee, R.W., Ebbert, J.C., Tesoriero, A.J., Inkpen, E.L., (2002) Forensic applications of nitrogen and oxygen isotopes in tracing nitrate sources in urban environments. Environ Forensic 3, 125–130. doi:10.1006/enfo.2002.0086.
- Silva, S.R., Kendall, C., Wilkison, D.H., Ziegler, A.C., Chang, C.C.Y., Avanzino, R.J., 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. Journal of Hydrology, 228, 22–36.
- Spivack, A.J., Edmond, J.M., 1986. Determination of boron isotope ratios by thermal ionization mass spectrometry of the dicesium metaborate cation. Anal. Chem., 58, 31-35.
- Tirez, K., Brusten, W., Widory, D., Petelet, E., Bregnot, A., Xue, D., Boeckx, P., Bronders, J., 2010. Boron Isotope Ratio (δ^{11} B) Measurements in Water

Framework Directive Programs: Comparison between Double Focusing Sector Field ICP and Thermal Ionization Mass Spectrometry, J. Anal. At. Spectrom. 25, 964-974.

- Travé, A., Labaume, P., Calvet, F., Soler, A. (1997) Sediment dewatering and pore fluid migration along thust faults in a foreland basin inferred from isotopic and elemental geochemical analyses (Eocene southern Pyrenees, Spain). Tectonophysics 282, 375-398.
- Vane, C.H., Kim, A.W., McGowan, S., Leng, M.J., Heaton, T.H.E., Kendrick, C.P., Coombs, P., Yang, H., Swann, G.E.A., 2010. Sedimentary records of sewage pollution using faecal markers in contrasting peri-urban shallow lakes. The Science of the Total Environment 409, 345-356.
- Van Stempvoort, D.R., Krouse, H.R., 1994. Controls of δ¹⁸O in sulphate. In: Alpers,
 C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulphide Oxidation.
 American Chemical Society, Washington, pp. 446–480.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron Isotope Application for Tracing Sources of Contamination in Groundwater. Environmental, Science and Technology 28, 1968-1974.
- Vilanova, E., 2004. Anàlisi dels sistemes de flux a l'àrea Gavarres-Selva-Baix
 Empordà. Proposta de model hidrodinàmic regional. Ph.D Dissertation.
 Universitat Autònoma de Barcelona, 337 pp.
 http://www.tdx.cat/handle/10803/3437
- Vilanova, E., Mas-Pla, J., Menció, A., 2008. Determinación de sistemas de flujo regionales y locales en las depresiones tectónicas del Baix Empordà y La Selva (NE de España) en base a datos hidroquímicos e isotópicos. Boletín Geológico y Minero, 119 (1), 51-62.

- Vitòria, L., 2004. Estudi multi-isotòpic (δ¹⁵N, δ³⁴S, δ¹³C, δ¹⁸O, δD i ⁸⁷Sr/⁸⁶Sr) de les aigües subterrànies contaminades per nitrats d'origen agrícola i ramader. Translated title: Multi-isotopic approach (δ¹⁵N, δ³⁴S, δ¹³C, δ¹⁸O, δD and ⁸⁷Sr/⁸⁶Sr) of nitrate contaminated groundwaters by agricultural and stockbreeder activities. PhD Thesis. Universitat de Barcelona, 188 pp.
- Vitòria, L., Otero, N., Canals, A., Soler, A., 2004. Fertilizer characterization: isotopic data (N, S, O, C and Sr). Environ. Sci. Technol. 38, 3254–3262.
- Vitòria, L., Soler, A., Aravena, R., Canals, A., 2005. Multi-isotopic approach (¹⁵N, ¹³C, ³⁴S, ¹⁸O and D) for tracing agriculture contamination in groundwater (Maresme, NE Spain). In: Environmental Chemistry (Eds. E. Lichtfouse, J. Schwarzbauer and D. Robert). Springer-Verlag, Heidelberg, 43-56.
- Vitòria, L., Soler, A., Canals, A., Otero, N., 2008. Environmental isotopes (N, S, C, O, D) to determine natural attenuation processes in nitrate contaminated waters: example of Osona (NE Spain). Appl. Geochem. 23, 3597–3611.
- Waldron, S., Tatner, P., Jack, I., Arnott, C., 2001. The Impact of Sewage Discharge in a Marine Embayment: A Stable Isotope Reconnaissance. Estuarine, Coastal and Shelf Science, 52, 111–115. doi:10.1006/ecss.2000.0731.
- Ward, M.H., deKok, T.M., Levallois, P., Brender, J., Gulis, G., Nolan, B.T., VanDerslice, J., 2005. Workgroup report: drinking-water nitrate and health recent findings and research needs. Environ. Health Perspect. 113, 1607–1614.
- Wassenaar, L. I., 1995. Evaluation of the origin and fate of nitrate in the Abbotsford aquifer using the isotopes of ¹⁵N and ¹⁸O in NO₃. Applied Geochemistry, 10, 391–405.

Widory, D., Kloppmann, W., Chery, L., Bonnin, J., Rochdi, H., Guinamant, J.L., 2004. Nitrate in groundwater: an isotopic multi-tracer approach. Journal of Contaminant Hydrology, 72, 165-188.

- Widory, D., Petelet-Giraud, E., Négrel, P., Ladouche, B., 2005. Tracking the sources of nitrate in groundwater using coupled nitrogen and boron isotopes: a synthesis.
 Environmental, Science and Technology, 39, 539-548.
- Widory, D., Petelet-Giraud, E., Brenot, A., Bronders, J., Tirez, K., Boeckx, P., 2013. Improving the management of nitrate pollution in water by the use of isotope monitoring: the δ^{15} N, δ^{18} O and δ^{11} B triptych. Isotopes in Environmental and Health Studies, 48, 1-19.
- Xu, S., Kang, P, Sun, Y., 2016. A stable isotope approach and its application for identifying nitrate source and transformation process in water. Environ Sci Pollut Res 23, 1133-1148.
- Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Research, 43, 1159-1170.
- Yingkai, X., Lan, W., 2001. The effect of pH and temperature on the isotopic fractionation of boron between saline brine and sediments. Chem. Geol. 171, 253–261.

Figure captions

Figure 1. Geological map of the Baix Ter basin, sampling point locations labelled according to the hydrogeological formation where they are located. Potentiometric contour lines of the unconfined aquifer, mainly in the shallow Quaternary formations, correspond to the August 2004 survey. Dashed line represents the zero elevation potentiometric level in the deep quaternary formations (mainly leaky aquifers) affected by intensive withdrawal rates in the central area of the basin. Geology from ICGC (http:// www.icgc.cat).

Figure 2. $\delta^{18}O_{H2O}$ and $\delta^{2}H$ of the Baix Ter groundwater samples collected in January 2004 (a) and August 2004 (b). The annual-Local Meteoric Water Line (LMWL) follows the equation $\delta^{2}H = 7.98(\pm 2.71) \delta^{18}O + 7.85(\pm 0.47)$ (r²=0.924, n=23) (Vilanova, 2004), whose slope is equal to that of the neighbouring areas ($\delta^{2}H = 7.9 \delta^{18}O + 9.8$; Neal et al., 1992).

Figure 3. Mn concentrations plotted against the Eh values of the groundwater samples. Eh ranges of MnO_2/Mn^{2+} and $NO_3^{-}/N_{2(g)}$ redox pairs are taken from Rivett et al. (2008).

Figure 4 a) NO₃⁻ concentration versus Cl⁻ concentration, b) NO₃⁻ concentration versus SO_4^{2-} concentration, c) SO_4^{2-} concentration versus (NO₃⁻/Cl⁻) ratio, and d) B concentration versus (NO₃⁻/Cl⁻) ratio.

Figure 5. a) Variations of the δ^{15} N and δ^{18} O of dissolved NO₃⁻ in groundwater according to their hydrogeological unit. Isotope ranges of the main NO₃⁻ sources listed in Table 4 are also represented. The extreme isotopic fractionation factors from the literature are $\epsilon_N/\epsilon_O = 2.1$ (Böttcher et al., 1990) and $\epsilon_N/\epsilon_O = 1.3$ (Fukada et al., 2003). b) $\delta^{18}O_{NO3}$ values plotted against $\ln(NO_3^-/CI^-)$ according to their hydrogeological unit. R² values for the linear regressions for shallow Quat. and deep Tert. Units are also reported.

Figure 6. δ^{34} S and δ^{18} O of dissolved SO₄²⁻ in groundwater according to their hydrogeological unit. Isotope ranges of natural and anthropogenic SO₄ sources listed in Table 4 are also represented. The area of sulphates derived from sulphide oxidation is from Van Stempvoort and Krouse (1994). Dashed lines define the isotopic fractionation range (ϵ^{34} S/ ϵ^{18} O_{SO4}) in SO₄ reduction reactions, varying between 2.5 and 4 (Mizutani and Rafter, 1973).

Figure 7. δ^{11} B values plotted against B concentration (a) and δ^{15} N values (b). Isotope ranges of the main NO₃⁻ sources listed in Table 4 are also represented. δ^{11} B_{seawater} is taken from Vengosh et al. (1994).

Figure 8. a) $\delta^{18}O_{NO3}$ values plotted against $\ln(NO_3^-/HCO_3^-)$. b) $\delta^{13}C_{HCO3}$ values plotted against HCO_3^- concentration. Isotope ranges of the main NO_3^- sources listed in Table 4 are also represented. Value for $\delta^{13}C_{HCO3}$ for marls is from Travé et al. (1997).

Table captions

Table 1. Hydrogeological formation, X and Y UTM coordinates, depth (m), hydraulic head (m.a.s.l.), and physico-chemical parameters measured in situ for the sampled points of each field campaign. See Fig. 1 for sampling locations in the Baix Ter basin.
R₁ and R₂ Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined).

Table 2. Hydrochemical data for the January and August 2004 field campaigns ("*" = DOC concentrations instead of TOC concentrations). R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined; *u.d.l.*: under detection limit).

Table 3. Isotope data for the January and August 2004 field campaigns. R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined).

Table 4. Ranges of nitrate, sulphate, boron and dissolved inorganic carbon isotope compositions of the main potential sources of nitrate obtained from the literature.

Table 1Click here to download Table: Table 1.docx

Table 1. Hydrogeological formation, X and Y UTM coordinates, depth (m), hydraulic head (m.a.s.l.), and physico-chemical parameters measured in situ for the sampled points of each field campaign. See Fig. 1 for sampling locations in the Baix Ter basin. R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined)

Sample	Field	Hydrogeological	X (UTM)	Y (UTM)	Depth	Hydraulic	Т	EC (25 °C)	pН	Eh
	campaign	formation			(m)	head	(°C)	(mS/cm)		(mV)
						(m.a.s.l.)				
Q ₁	1	Q _D	504970	4654520	28	13.1	14.0	787	7.9	89
Q_2	1	Q _D	508910	4653880	46	-1.4	14.4	596	8.0	46
Q ₃	1	Q _D	508790	4648620	72	16.9	16.7	955	7.7	397
Q2	2	Q _D	508910	4653880	46	-3.0	18.3	812	7.8	188
Q ₃	2	Q _D	508790	4648620	72	15.6	18.2	1225	7.7	393
Q4	1	Qs	506280	4653300	7	10.8	15.0	1594	7.4	276
Q5	1	Qs	502300	4649320	10	27.4	16.0	1640	7.6	376
Q_6	1	Qs	503340	4649390	10	22.4	14.6	899	7.6	332
Q ₇	1	Qs	501670	4655680	21	13.4	17.0	843	7.7	368
Q_8	1	Qs	504920	4656490	20	10.9	16.9	862	7.9	366
Q9	1	Qs	505460	4652860	10	12.6	14.0	772	7.9	267
Q ₁₀	1	Qs	504340	4644620	8	60.3	16.3	1180	7.7	425
Q ₁₁	1	Qs	507820	4647100	6	32.0	13.3	722	8.2	361
Q ₁₂	1	Qs	501970	4655900	20	12.3	16.1	773	7.9	340

Q ₁₃	1	Qs	504290	4652570	16	13.1	14.9	836	7.8	449
Q ₁₄	1	Qs	504920	4646740	6	37.7	13.2	886	8.2	378
Q ₁₅	1	Qs	509180	4650980	6	5.2	15.3	2523	7.6	409
Q ₁₆	1	Qs	510970	4644350	6	36.4	14.7	1004	7.8	392
Q ₅	2	Qs	502300	4649320	10	24.8	16.8	2359	7.6	386
Q_6	2	Qs	503340	4649390	10	n.d.	17.3	1125	7.8	318
\mathbf{Q}_7	2	Qs	501670	4655680	21	10.2	17.1	1164	7.5	413
Q_8	2	Qs	504920	4656490	20	10.7	17.7	1383	7.8	332
Q_9	2	Qs	505460	4652860	10	n.d.	16.2	1070	7.7	395
Q ₁₀	2	Qs	504340	4644620	8	60.4	16.2	1320	7.4	428
Q ₁₃	2	Qs	504290	4652570	16	8.7	16.2	1219	7.4	395
Q ₁₄	2	Qs	504920	4646740	12	36.1	17.6	949	7.5	365
Q ₁₅	2	Qs	509180	4650980	6	3.8	17.3	2993	8.0	388
Q ₁₆	2	Qs	510970	4644350	6	35.7	22.9	1007	7.8	443
Q ₁₇	2	Qs	501720	4647990	n.d.	29.5	17.6	809	7.9	386
Q ₁₈	2	Qs	510230	4648070	6	14.2	17.9	875	7.7	408
Q ₁₉	2	Qs	508410	4647030	12	32.8	16.4	999	7.6	348
Q ₂₀	2	Qs	503580	4647920	17	19.0	15.8	661	7.8	727
Q ₂₁	2	Qs	505090	4650800	17	15.0	16.2	980	7.5	445
S	1	spring	507650	4645200	0	55.0	15.0	629	7.7	319

S	2	spring	507650	4645200	0	55.0	15.4	748	7.9	334
T ₁	1	T _D	508930	4648350	90	21.6	19.5	552	8.0	348
T_2	1	T _D	508830	4651340	100	7.2	14.9	908	8.0	369
T_3	1	T _D	503340	4651590	100	27.7	17.5	1176	7.8	378
T_4	1	T _D	505912	4646025	110	27.4	16.6	725	8.1	n.d.
T_5	1	T _D	504420	4647820	125	27.1	16.5	1325	7.8	343
T_6	1	T _D	511510	4646260	110	-4.5	18.5	736	7.8	362
T ₁	2	T _D	508930	4648350	90	21.6	20.0	935	7.7	366
T_2	2	T _D	508830	4651340	100	11.4	19.8	1095	7.7	426
T_3	2	T _D	503340	4651590	100	22.1	17.2	1500	7.7	370
T_5	2	T _D	504420	4647820	125	24.4	19.1	1330	7.9	301
T_6	2	T _D	511510	4646260	110	-4.5	19.0	600	8.2	326
T_7	2	T _D	499910	4647360	70	42.0	21.2	1164	7.7	425
T_8	2	T _D	501790	4643590	156	n.d.	18.1	1374	8.0	357
T ₉	2	T_{D}	507880	4644460	85	53.9	18.4	971	7.9	157
T_{10}	2	T _D	510025	4649000	125	n.d.	20.7	1053	7.9	183
T ₁₁	2	T_{D}	501590	4647810	130	23.8	19.4	824	8.0	916
T ₁₂	2	T_{D}	498230	4653260	110	n.d.	19.3	994	7.8	456
T ₁₃	2	T_{D}	512180	4645340	175	n.d.	17.1	1137	7.6	393
T ₁₄	2	T _D	508150	4649930	60	19.3	17.0	1449	7.6	159

T ₁₅	2	T _D	501970	4653420	80	n.d.	19.1	1389	7.8	331
T ₁₆	1	Ts	510930	4647500	22	-6.5	16.1	1006	7.9	363
T ₁₆	2	Ts	510930	4647500	22	-5.8	16.8	1219	7.5	408
T ₁₇	2	Ts	502650	4652480	40	23.7	19.2	2414	7.6	321
T ₁₈	2	Ts	499460	4652480	34	126.0	18.0	837	8.0	357
T ₁₉	2	Ts	500770	4651700	10	106.3	17.8	944	8.0	352
T ₂₀	2	Ts	508550	4653010	9	9.0	17.7	1528	7.7	357
T ₂₁	2	Ts	504505	4643350	5	102.5	22.2	649	7.7	385
T ₂₂	2	Ts	499640	4645180	n.d.	n.d.	17.9	1055	7.6	327
T ₂₃	2	Ts	502340	4646230	40	35.0	17.5	1438	7.5	372
R ₁	-	Ter River	505699	4654685	-	-	n.d.	636	7.8	n.d.
R_2	-	Ter River	499361	4658519	-	-	n.d.	664	7.8	n.d.

Table 2. Hydrochemical data for the January and August 2004 field campaigns ("*" = DOC concentrations instead of TOC concentrations). R₁ and R₂ Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined; *u.d.l.*: under detection limit).

	Field	Hydrogeological	HCO ₃ ⁻	SO_4^{2-}	Cl	NO ₃ ⁻	Na^+	\mathbf{K}^+	Ca ²⁺	Mg^{2+}	$\mathrm{NH_4^+}$	TOC	Mn	Fe	В
Sample	campaign	formation	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Q_1	1	Q _D	413	66	138	u.d.l.	43	u.d.l.	157	23	0.15	1.2	0.056	0.015	u.d.l.
Q_2	1	Q _D	349	48	51	u.d.l.	44	3	90	19	0.47	1.0	0.289	0.020	u.d.l.
Q_3	1	Q _D	361	117	79	115	37	u.d.l.	181	18	0.15	1.2	0.002	0.010	u.d.l.
Q ₂	2	Q _D	341	41	61	u.d.l.	45	3	99	19	0.41	0.6	0.335	0.016	u.d.l.
Q ₃	2	Q _D	335	129	79	144	36	u.d.l.	184	17	0.14	0.9	0.002	u.d.l.	u.d.l.
Q4	1	Qs	473	227	269	6	92	4	239	40	0.25	2.3	4.380	0.019	0.127
Q ₅	1	Qs	463	223	200	215	88	u.d.l.	291	28	0.13	2.1	0.002	0.019	u.d.l.
Q_6	1	Qs	388	71	62	88	31	2	153	18	0.15	1.6	0.003	0.015	u.d.l.
\mathbf{Q}_7	1	Qs	353	111	76	48	30	u.d.l.	159	22	0.13	1.0	0.001	0.013	u.d.l.
Q_8	1	Qs	347	136	99	13	60	3	128	25	0.12	1.4	0.783	0.016	u.d.l.
Q ₉	1	Qs	372	86	84	25	63	4	122	17	0.16	1.2	0.002	0.012	0.217
Q_{10}	1	Qs	384	114	60	325	41	u.d.l.	245	15	0.18	1.3	0.001	0.014	0.113

Q ₁₁	1	Qs	253	60	52	31	31	3	94	13	0.17	3.3	0.003	0.018	u.d.l.
Q ₁₂	1	Qs	324	134	81	12	43	2	141	20	0.18	1.1	0.001	0.011	0.055
Q ₁₃	1	Qs	401	89	106	51	44	u.d.l.	167	20	0.15	1.9	0.001	0.017	0.089
Q ₁₄	1	Qs	210	77	52	147	29	u.d.l.	128	12	0.15	1.7	0.002	u.d.l.	u.d.l.
Q ₁₅	1	Qs	427	277	294	387	94	72	283	76	0.14	3.2	0.001	0.011	0.168
Q ₁₆	1	Qs	351	124	76	168	57	u.d.l.	183	19	0.17	1.9	0.001	u.d.l.	u.d.l.
 Q ₅	2	Qs	483	321	226	328	123	u.d.l.	331	30	0.14	1.6	0.001	u.d.l.	u.d.l.
Q_6	2	Qs	366	88	59	129	28	2	165	18	0.16	0.6	0.006	u.d.l.	u.d.l.
Q ₇	2	Qs	399	112	79	122	30	u.d.l.	201	26	0.11	0.5	0.001	0.011	u.d.l.
Q_8	2	Qs	337	204	139	51	71	3	174	31	0.08	1.1	0.971	u.d.l.	u.d.l.
Q ₉	2	Qs	358	86	84	26	58	4	130	17	0.11	0.6	0.002	u.d.l.	0.209
Q ₁₀	2	Qs	440	76	50	241	45	u.d.l.	225	13	0.12	0.9	0.002	0.012	0.189
Q ₁₃	2	Qs	405	120	86	66	44	2	178	21	0.08	1.2	0.001	u.d.l.	0.123
Q ₁₄	2	Qs	195	66	55	201	29	u.d.l.	140	13	0.08	0.5	0.002	0.011	u.d.l.
Q ₁₅	2	Qs	413	371	362	480	111	68	345	85	0.14	3.4	0.001	u.d.l.	0.150
Q ₁₆	2	Qs	356	93	55	65	47	u.d.l.	143	14	0.14	0.6	0.001	u.d.l.	u.d.l.

Q ₁₇	2	Qs	301	29	28	60	18	u.d.l.	116	12	0.13	0.4	0.001	u.d.l.	u.d.l.
Q ₁₈	2	Qs	390	102	47	83	38	6	163	14	0.13	0.6	0.001	u.d.l.	u.d.l.
Q ₁₉	2	Qs	304	55	52	205	24	u.d.l.	166	14	0.15	0.7	0.001	0.022	u.d.l.
Q ₂₀	2	Qs	177	52	52	50	29	5	83	11	0.12	0.9	0.001	0.012	0.082
Q ₂₁	2	Qs	313	95	71	45	55	4	124	16	0.21	0.6	0.002	0.011	0.232
S	1	spring	298	64	47	37	29	u.d.l.	110	12	0.18	1.4	0.001	0.011	u.d.l.
S	2	spring	268	58	50	68	31	u.d.l.	117	13	0.15	1.0	0.001	0.013	<i>u.d.l.</i>
T ₁	1	T _D	417	68	43	10	42	3	131	13	0.13	0.8	0.001	0.012	u.d.l.
T_2	1	T _D	470	156	87	9	51	3	129	54	0.13	1.3	0.018	0.019	u.d.l.
T ₃	1	T _D	276	116	123	222	55	u.d.l.	185	22	0.15	1.9	0.001	0.014	u.d.l.
T_4	1	T _D	383	110	60	15	33	49	118	24	0.16	1.2	0.025	0.016	0.071
T ₅	1	T _D	430	152	119	222	105	12	178	36	0.20	2.8	0.007	0.012	0.066
T_6	1	T _D	382	59	76	46	57	3	118	20	0.14	1.2	0.007	0.014	u.d.l.
T_1	2	T _D	402	55	41	23	35	3	136	12	0.16	0.4	0.001	u.d.l.	<i>u.d.l.</i>
T_2	2	T _D	435	157	74	11	44	3	127	51	0.12	0.7	0.026	u.d.l.	0.081
T ₃	2	T _D	376	91	180	221	68	4	214	30	0.12	1.7	0.001	u.d.l.	0.065

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		T_5	2	T_D	514	118	99	61	162	11	94	23	0.18	0.6	0.010	u.d.l.	0.104
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		T ₆	2	T _D	354	34	70	3	54	3	100	18	0.14	0.3	0.007	u.d.l.	0.051
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		T_7	2	T _D	368	83	66	139	32	u.d.l.	183	14	0.14	0.9	0.001	u.d.l.	u.d.l.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T_8	2	T _D	222	107	135	265	58	9	181	24	0.12	1.1	0.007	0.016	u.d.l.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T ₉	2	T _D	384	31	118	u.d.l.	75	5	81	39	0.16	0.9	0.197	0.013	0.055
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T ₁₀	2	T _D	533	74	52	u.d.l.	63	2	168	16	0.10	0.4	0.064	0.013	0.053
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T ₁₁	2	T _D	323	32	46	69	41	3	106	16	0.11	0.8	0.001	0.013	u.d.l.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T ₁₂	2	T _D	379	52	62	71	33	3	104	45	0.12	0.4	0.002	0.013	u.d.l.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T ₁₃	2	T _D	392	86	96	46	55	2	146	28	0.12	0.7	0.001	0.010	0.051
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		T_{14}	2	T _D	619	87	126	u.d.l.	74	4	102	94	0.33	0.5	0.042	0.016	0.061
T_{16} 2 T_s 3711461027149u.d.l.169320.230.90.0020.012		T ₁₅	2	T _D	401	95	130	152	114	3	110	42	0.21	1.2	0.002	0.014	0.095
T_{17} 2 T_s 37224523141912259223700.112.60.003u.d.l.0 T_{18} 2 T_s 249303114715u.d.l.121190.140.60.001u.d.l.10	-	T ₁₆	1	T _S	388	149	93	63	55	2	162	37	0.12	1.4	0.002	0.014	u.d.l.
T_{18} 2 T_{S} 249 30 31 147 15 <i>u.d.l.</i> 121 19 0.14 0.6 0.001 <i>u.d.l.</i>		T ₁₆	2	T _s	371	146	102	71	49	u.d.l.	169	32	0.23	0.9	0.002	0.012	u.d.l.
		T ₁₇	2	T _s	372	245	231	419	122	59	223	70	0.11	2.6	0.003	u.d.l.	0.084
T_{19} 2 T_{S} 348 56 39 89 33 7 137 13 0.14 1.2 0.003 <i>u.d.l.</i>		T ₁₈	2	T _s	249	30	31	147	15	u.d.l.	121	19	0.14	0.6	0.001	u.d.l.	u.d.l.
		T ₁₉	2	Ts	348	56	39	89	33	7	137	13	0.14	1.2	0.003	u.d.l.	u.d.l.

T ₂₀	2	Ts	350	210	108	212	56	6	200	38	0.17	2.2	0.001	u.d.l.	0.123
T ₂₁	2	Ts	300	30	36	6	22	u.d.l.	104	9	0.14	1.0	0.002	0.012	u.d.l.
T ₂₂	2	Ts	371	81	49	153	29	u.d.l.	193	8	0.16	1.1	0.002	0.012	u.d.l.
T ₂₃	2	Ts	355	66	181	190	75	u.d.l.	216	24	0.26	0.7	0.004	0.010	u.d.l.
R ₁	-	Ter River	194	73	50	7	38	5	75	11	n.d.	4.3*	0.029	0.010	0.075
R_2	-	Ter River	204	74	50	9	40	5	78	12	n.d.	4.5*	0.025	0.012	0.090

Table 3. Isotope data for the January and August 2004 field campaigns. R_1 and R_2 Ter River samples are from the Colomers station, NW of the study zone (Fig. 1). (*n.d.*: Not determined).

Sample	Field	Hydrogeological	δ ¹⁸ O-H ₂ O (‰)	δ ² H (‰)	δ ¹⁵ N (‰)	δ^{18} O-NO ₃ (‰)	$\delta^{34}S$ (‰)	δ^{18} O-SO ₄ (‰)	δ ¹³ C-DIC (‰)	$\delta^{11}B$ (‰)
	campaign	formation								
Q1	1	Q _D	-5.2	-35.8	n.d.	n.d.	14.7	16.1	-14.9	n.d.
Q ₂	1	Q _D	-5.5	-37.8	n.d.	n.d.	13.9	13.6	-13.7	n.d.
Q ₃	1	Q _D	-5.4	-35.4	11.6	8.3	0.4	5.6	-13.6	n.d.
Q ₂	2	Q _D	-5.9	-37.6	n.d.	n.d.	10.3	12.4	-13.8	n.d.
Q ₃	2	Q _D	-5.5	-34.9	12.3	8.4	0.9	5.5	-13.7	n.d.
Q4	1	Qs	-5.1	-33.6	32.5	18.1	8.2	13.0	-13.2	34.5
Q5	1	Qs	-5.3	-34.6	15.9	8.9	12.2	10.1	-12.9	n.d.
Q_6	1	Qs	-5.3	-33.9	11.3	6.8	6.2	6.8	-13.2	n.d.
Q ₇	1	Qs	-6.0	-40.8	12.2	7.7	6.3	7.8	-11.3	n.d.
Q_8	1	Qs	-6.5	-44.1	20.5	13.7	9.1	10.1	-12.7	n.d.
Q ₉	1	Qs	-5.4	-35.3	19.1	10.1	6.8	8.9	-14.0	23.3
Q ₁₀	1	Qs	-5.8	-39.5	10.4	4.4	5.9	4.8	-12.5	25.7

Q ₁₁	1	Qs	-6.3	-39.6	13.6	8.7	5.1	7.8	-16.0	n.d.
Q ₁₂	1	Qs	-6.3	-41.9	13.3	8.1	8.2	8.9	-12.4	26.0
Q ₁₃	1	Qs	-5.3	-35.9	14.7	9.2	6.3	8.2	-13.9	28.3
Q ₁₄	1	Qs	-5.6	-36.8	7.7	5.5	4.0	5.4	-11.3	n.d.
Q ₁₅	1	Qs	-4.8	-31.8	13.5	7.5	2.6	5.8	-14.6	30.4
Q ₁₆	1	Qs	-5.5	-36.9	8.7	4.2	5.3	5.3	-14.0	n.d.
 Q5	2	Qs	-5.3	-33.5	18.9	5.3	12.7	10.2	-15.5	n.d.
Q ₆	2	Qs	-5.3	-33.8	12.3	7.2	6.1	7.0	-13.6	n.d.
Q ₇	2	Qs	-5.3	-36.3	12.3	6.5	3.0	6.0	-12.0	n.d.
Q_8	2	Qs	-6.6	-43.9	16.3	9.5	8.0	7.8	-11.8	n.d.
Q ₉	2	Qs	-5.5	-34.8	21.6	10.6	7.7	9.9	-14.1	n.d.
Q ₁₀	2	Qs	-6.0	-40.6	13.4	4.6	6.4	5.1	-16.0	n.d.
Q ₁₃	2	Qs	-5.3	-33.8	15.7	9.1	5.9	8.5	-13.6	n.d.
Q ₁₄	2	Qs	-5.2	-34.8	9.9	4.4	4.6	5.0	-14.7	n.d.
Q ₁₅	2	Qs	-4.9	-31.8	16.2	4.6	3.3	5.3	-14.1	n.d.
Q ₁₆	2	Qs	-5.8	-37.3	7.2	4.3	4.7	6.1	-14.1	n.d.

Q ₁₇	2	Qs	-5.4	-35.6	8.4	4.8	7.2	6.6	-15.0	n.d.
Q ₁₈	2	Qs	-5.6	-38.0	8.2	4.5	-1.4	6.3	-12.2	n.d.
Q ₁₉	2	Qs	-5.5	-38.2	10.5	5.5	3.1	4.9	-13.4	n.d.
Q ₂₀	2	Qs	-5.6	-36.2	13.6	7.4	5.6	6.6	-14.9	9.0
Q ₂₁	2	Qs	-5.6	-36.9	16.6	9.9	5.4	7.5	-14.7	1.4
S	1	spring	-5.8	-37.4	8.6	5.0	5.3	7.3	-14.3	n.d.
S	2	spring	-5.9	-37.7	9.6	6.8	5.4	7.2	-13.5	n.d.
T ₁	1	T _D	-5.6	-37.8	8.9	6.8	1.6	8.2	-10.2	n.d.
T_2	1	T _D	-5.2	-35.1	16.0	8.0	-13.5	3.8	-9.0	n.d.
T ₃	1	T _D	-5.1	-33.1	7.6	4.7	4.9	6.0	-13.7	n.d.
T_4	1	T _D	-5.5	-36.3	14.9	10.1	4.9	10.1	-13.3	31.7
T ₅	1	T _D	-5.3	-34.7	11.1	5.3	4.2	4.8	-12.5	23.9
T_6	1	T_{D}	-5.6	-35.7	12.8	6.9	2.3	8.0	-12.0	n.d.
T ₁	2	T _D	-5.8	-36.4	10.8	6.8	1.5	7.6	-11.2	n.d.
T_2	2	T _D	-5.3	-35.3	22.6	10.9	-13.4	4.2	-9.1	n.d.
T ₃	2	T _D	-5.2	-36.1	11.0	7.0	5.5	6.2	-13.9	n.d.

Т	5	2	T _D	-5.9	-37.5	13.7	6.5	5.8	7.9	-8.5	n.d.
Т	6	2	T _D	-5.9	-37.1	12.1	9.1	-2.6	11.1	-11.9	n.d.
Т	7	2	T _D	-5.5	-36.3	10.8	5.2	5.2	6.6	-13.4	n.d.
Т	8	2	T _D	-5.6	-35.7	13.8	6.1	5.3	4.6	-15.4	n.d.
Т	9	2	T _D	-6.1	-39.0	n.d.	n.d.	14.2	12.0	-11.5	n.d.
Т	10	2	T _D	-5.7	-37.6	n.d.	n.d.	10.0	10.6	-10.2	n.d.
Т	11	2	T _D	-5.4	-39.7	11.6	6.6	6.3	6.2	-13.0	n.d.
Т	12	2	T _D	-5.2	-37.5	13.8	7.1	-1.8	4.5	-12.1	n.d.
Т	13	2	T _D	-5.7	-37.6	11.9	5.6	1.7	5.8	-12.5	n.d.
Т	14	2	T _D	-5.4	-36.4	n.d.	n.d.	-16.0	4.9	-6.5	n.d.
Т	15	2	T _D	-5.4	-36.6	12.2	5.0	6.2	5.2	-13.1	n.d.
Т	16	1	T _S	-5.4	-34.8	10.7	8.5	-4.1	5.8	-11.3	n.d.
T	16	2	T _S	-5.0	-35.1	13.3	9.4	-1.7	5.5	-11.9	n.d.
Т	17	2	T _s	-5.1	-34.3	16.1	1.8	5.9	6.3	-14.5	29.5
Т	18	2	T _s	-5.0	-33.9	6.3	3.5	4.1	5.0	-13.5	n.d.
Т	19	2	Ts	-5.9	-38.1	9.3	6.2	7.3	9.2	-16.2	n.d.

T ₂₀	2	Ts	-5.4	-36.0	12.2	5.1	3.3	5.6	-13.2	25.5
T ₂₁	2	Ts	-6.2	-36.8	5.0	6.3	6.9	5.1	-14.9	n.d.
T ₂₂	2	Ts	-5.7	-36.2	11.5	6.2	6.6	4.9	-15.6	n.d.
T ₂₃	2	Ts	-5.6	-38.2	16.1	6.1	9.4	4.3	-14.8	n.d.
R ₁	-	Ter River	n.d.	n.d.	13.2	4.2	11.3	9.5	n.d.	n.d.
R_2	-	Ter River	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 4. Ranges of nitrate, sulphate, boron and dissolved inorganic carbon isotope compositions of the main potential sources of nitrate obtained from the literature.

NO ₃ ⁻ source Isotope ratio (‰)	Pig manure	Mineral fertilizers	Sewage	Soil
	+8 - +16	-4 +8	+5 +20	+3 +8
$\delta^{15}N$	Vitòria (2004)	Michalski et al. (2015), Vitòria et al. (2004)	Aravena and Mayer (2010), Curt el al. (2004), Vane et al. (2010)	Aravena and Mayer (2010), Heaton (1986), Kendall et al. (2007)
$\delta^{18}O_{NO3}$	+3.4 — +4.6 Estimated in this study	+17 — +25 Aravena and Mayer (2010), Vitòria	+3.4 — +4.6 Estimated in this study	+3.4 — +4.6 Estimated in this study
	according to eq.5	et al. (2004), Xue et al. (2009)	according to eq.5	according to eq.5
δ^{34} S	-0.9 +5.8	0 +10	+7.6 - +11.7	0 — +6
	Cravotta (1997)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)
	+3.8 - +6	+9 +15	+9 +11.1	0 — +6
$\delta^{18}O_{SO4}$	Otero et al. (2007), Vitòria (2004)	Vitòria et al. (2004)	Otero et al. (2008)	Krouse and Mayer (2000)

	+19.5 - +42.4	-9 -+ +15	-7.7 — +12.9	-
$\delta^{11}B$		Komor (1997), Widory et al.		
	Widory et al. (2005)	· · · ·	al. (1994), Widory et al. (2013),	-
		(2005), (2013)	Xue et al. (2009)	
	-23.816.4	-35 — -24	-25 — -13	-23
$\delta^{13}C_{HCO3}$	Cravotta (1997), Vitòria		Jurado et al. (2013), Li et al.	$C_{1} = 1 = 1 = 1 = 1 = (1007)$
	(2004)	Vitòria et al. (2004)	(2010), Waldron et al. (2001)	Clark and Fritz (1997)

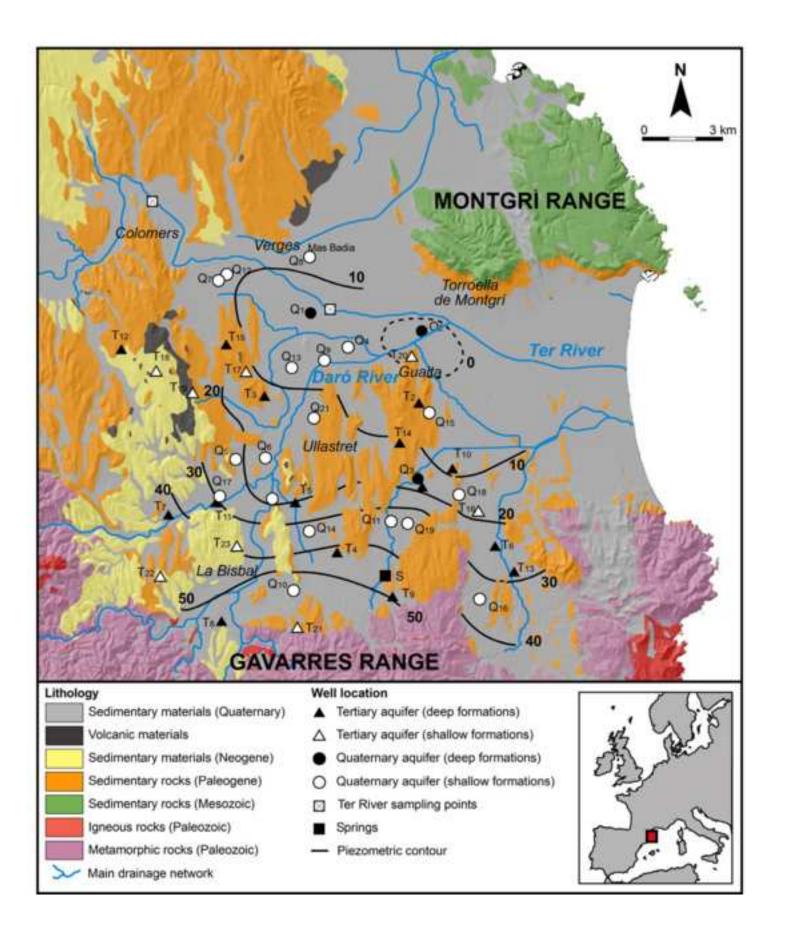


Figure 2 Click here to download Figure: figure2.docx

