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Combining boron isotopes and carbamazepine to trace sewage in salinized groundwater:
a case study in Cap Bon, Tunisia

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Abstract

The Korba aquifer on the east coast of Cape Bon has been overexploited since the 1960s with a resultant reversal of the hydraulic gradient and a degradation of the quality due to seawater intrusion. In 2008, the authorities introduced integrated water resources planning based on a managed aquifer recharge with treated wastewater. Water quality monitoring was implemented in order to determine the different system components and trace the effectiveness of the artificial recharge. Groundwater samples taken from recharge control piezometers and surrounding farm wells were analyzed for their chemical contents, for their boron isotopes, a proven tracer of groundwater salinization and domestic sewage, and their carbamazepine content, an anti-epileptic known to pass through wastewater treatment and so recognized as a pertinent tracer of wastewater contamination.

The system equilibrium was permanently disturbed by the different temporal dynamics of continuous processes such as cation exchange, and by threshold processes linked to oxidation-reductive conditions. The boron isotopic compositions significantly shifted back-and-forth due to mixing with end-members of various origins. Under the variable contribution of meteoric recharge, the Plio-Quaternary groundwater ($\delta^{11}\text{B}$ of 35-40.6‰, a mean B concentration of 30 $\mu\text{mol/L}$, no carbamazepine, $n=7$) was subject to seawater intrusion that induced a high $\delta^{11}\text{B}$ level ($\delta^{11}\text{B}$ of 41.5-48.0‰, a mean B concentration of 36 $\mu\text{mol/L}$, and $n=8$). Fresh groundwater ($\delta^{11}\text{B}$ of 19.89‰, B concentration of 2.8 $\mu\text{mol/L}$, no carbamazepine) was detected close to the recharge site and may represent the deep Miocene pole which feeds the upper Plio-Quaternary aquifer. The

managed recharge water ($\delta^{11}\text{B}$ of 10.67–13.8‰, $n=3$) was brackish and of poor quality with a carbamazepine content showing a large short term variability with an average daily levels of 328 ± 61 ng/L. A few piezometers in the vicinity of the recharge site gradually acquired a B isotopic composition close to the wastewater signature and showed an increasing carbamazepine content (from 20 to 910 ng/L). The combination of boron isotopic signatures with boron and carbamazepine contents is a useful tool to assess sources and mixing of treated wastewaters in groundwaters. Effluent quality needs to be greatly improved before injection to prevent further degradation of groundwater quality.

1 Introduction

The groundwater resources of coastal areas are highly vulnerable, being located either in complex hydrogeological structures or in local shallow aquifers where water stress and salt water intrusion occur under the multiple constraints governed by increasing anthropogenic pressures and climatic conditions (e.g. Custodio, 2002; de Montety et al., 2008; Pulido-Leboeuf, 2004...). Growing populations (both permanent and temporary, e.g. tourism) and activities have a negative effect on water resources through overexploitation and soil occupation. Also climate change, especially in semi-arid and arid regions, with its accentuated spatial and temporal variability of climatic phenomena, will strongly impact groundwater in both quantitative and qualitative terms. Yet, mitigation and adaptation measures in coastal zones should be carefully considered as it moreover addresses governance, health risks, and public perception. Recent integrated water resources planning often relies on alternative water supplies such as desalinization plants, managed aquifer recharge (MAR), aquifer storage and recovery (ASR), possibly completed with soil aquifer treatment (SAT) (e.g. Bouwer et al., 1990; Dillon et al., 2006...).

The coastal aquifer of the Cap Bon Peninsula in Tunisia is a typical case of groundwater depletion and seawater intrusion under a semi-arid climate due to the large quantities of water abstracted by the agricultural and industrial sectors since the 1960s (Ennabli, 1980; Kerrou et al., 2010; Paniconi et al., 2001b; Zghibi et al., 2011). The aquifer had thus become highly vulnerable, along with tourism, and urban and rural development. Managed aquifer recharge using treated wastewater was settled in 2008.

Recent works have used chemical tracers to identify seawater intrusion (Kouzana et al., 2009; 2010; Slama, 2010) with stable isotopes (Ben Hamouda et al., 2011; Ben Moussa et al., 2009). Our approach completes these studies by adding boron isotopes and carbamazepine to study the combined effects of abstraction, natural recharge, seawater intrusion, and artificial recharge, on groundwater dynamics.

Boron has two stable isotopes. Part of the dissolved B is removed from groundwater by surface adsorption on aquifer matrix minerals in its tetrahedral form, $^{10}\text{B}(\text{OH})_4^-$ which leads to an enrichment of the solution in residual ^{11}B leading to $\delta^{11}\text{B}$ increase, favored by neutral to slightly alkaline pH conditions (Goldberg and Suarez, 2011). Boron adsorption concerns a variety of exchange phases such as clay minerals, metal (hydr)oxides, organic matter and carbonates such as calcite (Goldberg and Forster, 1991; Majidi et al., 2010). In order to evaluate the recharge impact on groundwater quality and to elucidate the origins of groundwater salinization and pollution problems, boron isotopes have been used frequently since the 1990s (e.g. Pennisi et al., 2006; 2009; Vengosh et al., 1991, 1994, 2005). Boron is a good tracer of domestic wastewater because of the concentrations of Na- and Ca-perborates from washing powders with a well-defined B isotope signature and high B concentrations commonly exceeding 0.1 mmol/L (e.g. Barth, 1998; Vengosh et al., 1994...). In the context of artificial recharge, boron isotopes have been used in particular in the Dan region (Kanarek and Michail, 1996; Vengosh et al., 1994) where they enabled identification of the injectate plume at the scale of a MAR system (Kloppmann et al., 2008).

Similarly carbamazepine (CBZ), an everyday anti-epileptic drug whose lowest therapeutic dose is 200 mg/day (Cunningham et al., 2010), has been considered as a qualified parameter for detecting wastewater in the aquatic environment and is now used as a wastewater and artificial-recharge tracer (Clara et al., 2004). It is neither degraded nor subject to adsorption nor removed during wastewater treatment (Clara et al., 2004; Zhang et al., 2008). Its persistence, dissemination and the quantity used make it one of the most detected pharmaceuticals in the environment (Drewes et al., 2002; 2003; Fram and Belitz, 2011; Gasser et al., 2011; Heberer and Adam, 2004; Maeng et al., 2011; Schmidt et al., 2007). The CBZ molecule is polar and its neutrality at environmental pHs implies limited interaction with the generally negatively-charged mineral surfaces in aquifer materials (Fram and Belitz, 2011). The main phase that induces adsorption interactions is soil organic matter (SOM) (Chefetz et al., 2008; Maoz and Chefetz, 2010) due to the role of dissolved organic matter (DOM) (Navon et al., 2011). Thus its adsorption coefficient is rather low (0.21 to 5.32) in sandy sediments (Scheytt et al., 2005). The influx of dissolved organic matter originating from treated wastewater affects the behavior of organic pollutants and as such, CBZ and its metabolites are easily transported in the unsaturated and in the saturated zone when treated wastewater is used for irrigation or artificial aquifer recharge. CBZ is conservative under SAT conditions, and is not significantly degraded over years under aerobic nor anaerobic conditions (Arye et al., 2011; Gasser et al., 2010); it is even found preserved in groundwater after long flow times within the subsurface zone (Kreuziner et al., 2004). The multitracer

approach using CBZ and boron concentrations has already proven efficient (Katz et al., 2009; Rabiet et al., 2006).

In this article we describe groundwater contamination by salinization and anthropogenic activities, e.g. artificial recharge, taking into account spatial and temporal trends. We chemically trace the infiltration of poor quality treated wastewater by combining the isotopic signatures of dissolved boron and the concentrations of carbamazepine to assess the groundwater/treated wastewater mixing and groundwater contamination.

2 Study area

2.1 Geographic and climatic context

The east coast aquifer of the Cap Bon Peninsula, which lies 100 km east of Tunis, extends for about 45 km and underlies an area of approximately 475 km² (Figure 1). The region has a semi-arid climate characterized by an average annual rainfall of 480 mm with temporal irregularities. The climatic deficit covers a period of about 10 months and its maximum coincides with the period of drought.

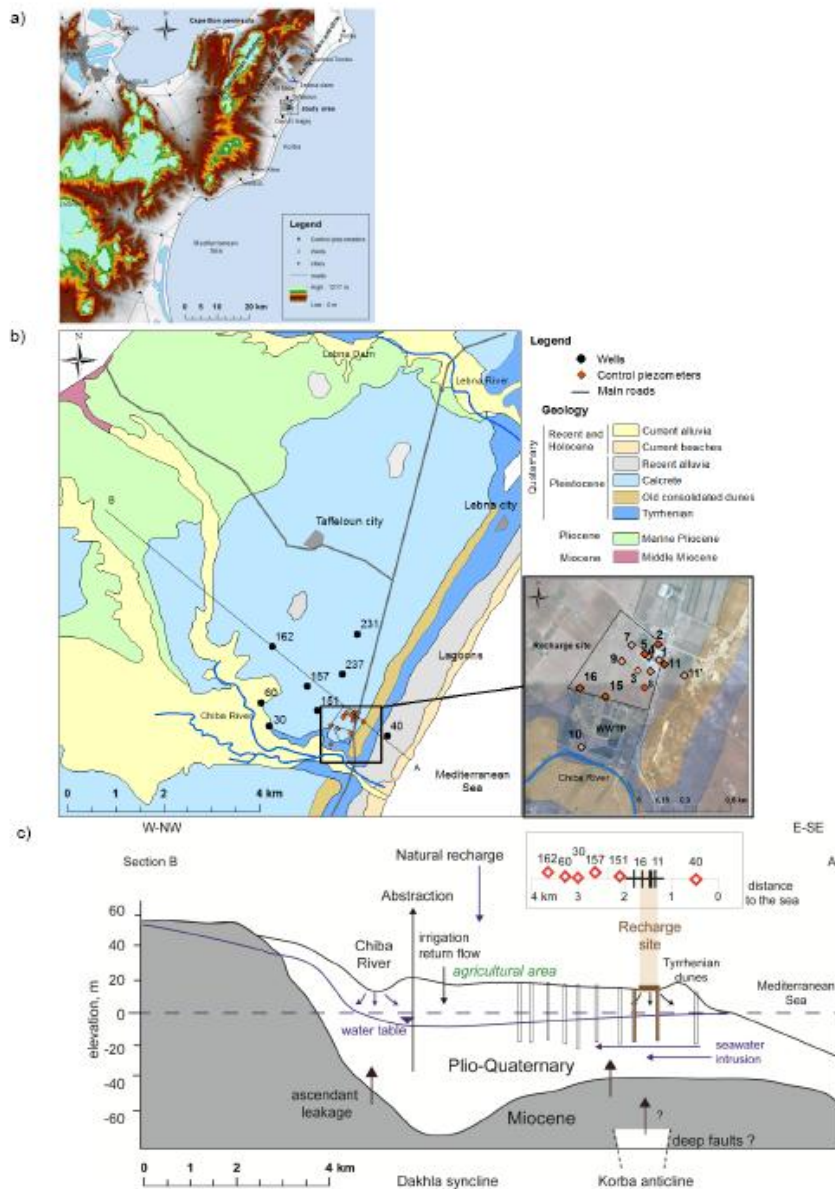


Figure 1: a) Location map of the Korba site in the Cap Bon Peninsula. The ASTER GDEM numerical model is a product of METI and NASA., b) Geological setting of the Korba-Ei Mida basin showing control-piezometer and farm-well sampling points (adapted from Archambault et al. (1947)), the satellite image was obtained from Google Earth; c) Schematic geological cross-section (AB) through the study area showing the locations of the recharge site, studied wells and piezometers (adapted from Zghibi et al. (2011)).

2.2 Geological settings

The Korba-Mida aquifer is made up mainly of marine sediments deposited in the Dakhla syncline north of Korba city (Abbes and Polak, 1981) (Fig. 1a). The study area is bounded to the north by Wadi Lebna, to the

south by Wadi Sidi Othmen, to the west by the elevated mountains consisting of Mio-Pliocene sequences, and to the east by the Mediterranean Sea. It is underlain mainly by Pliocene formations and Quaternary marine platforms.

(1) The Middle Miocene is the base of the system and is not exposed except some relics North West of the study area. It is 2700 m thick and is made up by detrital deposits mainly from deltaic bodies. The upper part is composed of lenticular sandstones and marls with lignite levels and clay in the study area (in red in Fig. 1b) truncated by riverine systems (Abbes and Polak, 1981) with a thickness of 500 m.

(2) Marine Pliocene sediments transgress unconformably the Miocene (in green in Fig. 1b) and outcrop North West of Taffeloun. These are composed mainly of interbedded sandstone-sand-marl topped with variably clayey sandstone with a thickness varying between 15 and 160 m (Ben Salem, 1992).

(3) Quaternary deposits in our study site contain upper Pleistocene and Holocene deposits. It can reach 150 m in the Taffeloun area. At the base, the upper Pleistocene deposits with a thickness of 30 m, also called Tyrrhenian deposits of the last marine transgression, are made up with fossiliferous carbonated sandstones and covered by old consolidate dunes with fossiliferous limestone (Fig. 1b). The further Pleistocene deposits, described as three marine platforms, show mixed carbonate, bioclastic and siliciclastic sediments (Elmejdoub and Jedoui, 2009; Temani et al., 2008). This facies is truncated by a carbonate sequence and aeolian oolitic deposits. The uppermost continental Pleistocene is represented by continental red deposits and a centimeter-to meter-thick calcrete extending over large areas (Ben Hamouda et al., 2011; Chakroun et al., 2005; Elmejdoub and Jedoui, 2009). At Taffeloun, the calcrete outcrops and its thickness is 15m (in clear blue in Fig 1b). The late Holocene deposits are represented by the recent alluvium of Wadi Chiba, by sabkha deposits and by the current beaches and dunes.

2.3 Hydrogeological setting and modeling

In our site, the aquifer system is constituted by the superficial and shallow Plio-Quaternary formations and by the deeper Miocene units.

The Miocene base is constituted by impermeable marls and contains brackish water with a salinity of 3 to 4 g/L (Rekaya, 1989). The younger upper Miocene is actively pumped at 150 to 500 m depth upstream of the study site and is tapped for drinking-water supply well in Taffeloun. The deep Miocene aquifer is captive and feeds the upstream Plio-Quaternary; its natural outlet is the sea. The relationship between both deep Miocene and Plio-Quaternary aquifers is known but not clear (Zghibi et al., 2011).

With no distinction in hydraulic terms, the Pliocene and Quaternary deposits form the Plio-Quaternary aquifer. According to electric sections, the Pliocene part contains a succession of saturated freshwater and brackish-water levels with, at the bottom, layers saturated with variably salty water (Kouzana et al., 2010). It is locally semi-confined due to less permeable deposits (Kerrou et al., 2010), and is the most productive aquifer of the area. Its recharge is provided by direct infiltration of rainwater and stream water. It is severely affected by salinization from seawater intrusion. The Quaternary part is vertically compartmentalized in places. Its recharge occurs principally through incised glacis and outcrops and is favored by the topographic relief formed by Quaternary Tyrrhenian fossil dunes. The main coastal sabkhas are no longer the natural outlets of the Tyrrhenian, due to a reversal of the hydraulic gradient.

The water balance is as follows: rainwater infiltration and irrigation recharge are estimated at around 18 Mm³/year (Kerrou et al., 2010), direct infiltration from wadis and dams reaches nearly 8 Mm³/year. Pumped abstraction of the groundwater by 2008 was estimated at 50 Mm³, (Ennabli, 1980; Kerrou et al., 2010; Paniconi et al., 2001a) which is two times the total recharge. Overexploitation induces piezometric depletion and seawater intrusion leading to salinization of groundwater.

2.4 Managed aquifer recharge through infiltration of treated wastewater

In order to provide a hydraulic barrier against seawater intrusion, the treated wastewater is infiltrated through ponds and undergoes soil aquifer treatment to improve its quality. The Korba-Mida artificial recharge site lies 15 m above sea level (NGT) and contains three infiltration basins, of which two function simultaneously. The monthly volume of water injected into the basins has ranged from 6,000 m³ to 37,653 m³ with a total of about 1.15 Mm³ of injected treated wastewater between December 2008 and March 2012. The treatment plant receives both urban wastewater and industrial wastewater from some 50 factories, mainly tomato or fish processing plants, but also slaughterhouses, and steel and tissue washing plants. The plant treatment consists on pre-treatment, secondary treatment by an oxidation channel process, and tertiary treatments performed with maturation ponds (El Ayni et al., 2011).

3 Material and methods

3.1 Water sampling, field and laboratory measurements

Groundwater samples for ion, B-isotope, and CBZ analyses were collected from control piezometers and private wells around the recharge area north of Wadi Chiba in June 2009, July 2010, and July 2011. Not all the farm wells are equipped with a pump and in these cases the samples were taken with a bucket from the bottom of the well. Although Well 231 was actively pumped, the samples were still taken at the bottom of the well because of long tubing. The other samples were taken directly at the exit of active pump (wells 157, 160, 161, 165, 173, Fig. 1).

pH, electrical conductivity, and temperature were measured in situ, as were piezometer levels. Alkalinity was measured in the laboratory one week after sampling. The major cations were determined by ICP-AES (10% uncertainty) and the anions (Br^- , F^- , Cl^- , SO_4^{2-} , NO_3^-) by ion chromatography (Dionex) (10% uncertainty). Metals and other minor elements were measured by ICP-MS (10% uncertainty). NH_4^+ was analysed by FFA and spectrometric detection. Nitrites were analysed by molecular absorption spectrometry (NF EN 26777). Bicarbonates and carbonates were analysed by potentiometry (NF EN ISO 9963-1).

3.2 Boron isotopes

Boron isotopic compositions were determined following the method described by Millot et al. (2011) using the positive-TIMS Cs_2BO_2 technique. The values were plotted on the δ scale (expressed in ‰) relative to the NBS951 boric acid standard, where the δ value is defined as:

$$\delta^{11}\text{B} (\text{‰}) = [((^{11}\text{B}/^{10}\text{B})_{\text{sample}} / (^{11}\text{B}/^{10}\text{B})_{\text{standard}}) - 1] * 10^3.$$

The $^{11}\text{B}/^{10}\text{B}$ of replicates analysis of the NBS951 boric acid standard after oxygen correction was 4.05133 ± 0.00107 (2σ , $n = 99$) during this period. The reproducibility of $\delta^{11}\text{B}$ determination was $\pm 0.3\text{‰}$ (2σ) and the internal uncertainty better than 0.2‰ ($2\sigma_m$). The accuracy and reproducibility of the procedure were verified by repeated measurements of the IAEA-B1 seawater standard for which the mean $\delta^{11}\text{B}$ value obtained over a long period is $+39.19\text{‰} \pm 0.34$ (2σ , $n=67$), in agreement with the accepted value for seawater.

3.3 Carbamazepine

Raw groundwater samples were filtrated before measurement in the lab. Carbamazepine in the water samples was measured at the BRGM. Analytical determination was performed using on line Solid-Phase Extraction

coupled with LC-ESI-MS/MS system. The carbamazepine quantification limit was 20 ng/L. The molecule is presented in Fig. 2.

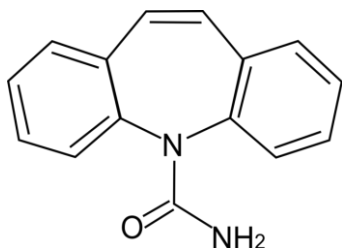
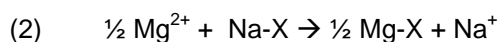
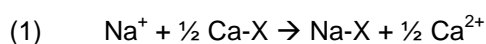


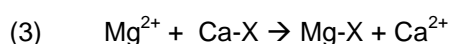
Figure 2: Carbamazepine structure.

3.4 Cationic exchange

Where the seawater intrusion is concerned, ion exchange is the mechanism by which the fine fraction of the sedimentary aquifer matrix, with its large surface area and high cation-exchange capacity, is able to influence the ion concentration and isotopic composition of the groundwater (Anderson and Smith, 2005; Appelo and Postma, 2005; de Montety et al., 2008; Pennisi et al., 2006...). A calcium and magnesium excess with a sodium deficit relative to the ideal mixing with seawater is typical of cation exchange processes with the fine fraction of the aquifer sediments according to the following reactions:



where X is the sediment exchanger (Appelo and Postma, 1993). The exchange phase in the aquifer comprises clay, organic matter, carbonates and even oxyhydroxides. Magnesium can also replace calcium on the exchanger according to following equation (3):



The calculation of the salinization rate is described in detail in the Supporting Information and values are given in Table 2A.

4 Results

The chemical parameters determined from the 2009, 2010 and 2011 water samples are shown in Table 1 and Fig. 3 and 4.

Table 1: Physical and chemical parameters of the water samples from wells, piezometers and Korba treatment plant, sampled in 2009, 2010 and 2011, and saturation indexes for calcite and dolomite. The saturation indexes of gypsum and halite are not given because all the samples were subsaturated between -0.5 and -2 (gypsum) and -4 and -6 (halite). ql is the quantification limit. TWW is for treated wastewater. The chemical results were of good quality with an error of <5.4% on the electrical balance.

Sample	Date	CE μS/cm	pH	Al μmol/L	Br mmol/L	Ca mmol/L	Cl mmol/L	HCO ₃ mmol/L	K mmol/L	Mg mmol/L	Mn μmol/L	Na mmol/L	NH ₄ mmol/L	NO ₂ mmol/L	NO ₃ mmol/L	SO ₄ mmol/L	H ₄ SiO ₄ mmol/L	Sr μmol/L	B μmol/L	δ ¹¹ B ‰	± 2σ _m ‰	Calcite SI	Dolomite SI
WWTP	15/06/2009	5150	8.35	3.31	0.023	3.71	32.98	8.02	1.03	2.97	2.250	34.19	1.128	0.2717	0.02	5.18	0.28	43.94	64.49	13.85	0.08	1.109	2.36
Piez 2	15/06/2009	11950	7.75	0.13	0.114	7.31	88.43	6.38	1.44	7.99	0.160	74.99	0.005	0.0004	2.24	6.99	0.25	49.69	62.36	31.1	0.08	-0.097	0.01
Piez 5	15/06/2009	5760	7.90	0.14	0.05	4.59	42.00	4.72	0.74	3.98	0.290	35.93	0.006	0.0007	1.71	3.84	0.44	36.48	34.41	33.35	0.08	-0.248	-0.41
Piez 8	15/06/2009	5720	7.95	0.20	0.053	4.97	42.68	3.57	0.84	3.44	0.130	34.49	0.003	0.0004	1.26	3.59	0.22	55.42	38.95	30.44	0.16	-0.145	-0.29
Piez 11	15/06/2009	16070	7.85	0.20	0.199	9.57	139.94	4.90	1.74	13.30	0.160	123.14	0.007	0.0024	1.73	11.03	0.28	60.82	51.21	44.98	0.12	-0.239	-0.17
Piez 15	15/06/2009	2880	7.95	0.11	0.016	3.08	17.52	4.44	0.69	1.56	0.260	18.14	0.003	0.0007	0.37	2.63	0.27	16.31	45.42	16.02	0.09	1.128	2.12
Piez 16	15/06/2009	5300	7.75	0.13	0.053	6.84	40.73	4.57	0.41	3.53	0.330	27.58	0.004	0.0124	0.88	2.46	0.26	31.20	20.79	29.78	0.16	-0.154	-0.43
60	15/06/2009	5190	7.35	0.21	0.043	10.74	34.81	2.67	0.30	4.70	0.010	20.27	0.005	0.0002	5.18	4.26	0.30	37.66	17.73	34.97	0.06	-0.945	-2.08
151	15/06/2009	8610	7.25	0.06	0.099	12.68	70.52	3.92	0.32	6.72	0.004	44.80	< ql	< ql	2.71	3.66	0.34	46.33	20.39	37.78	0.07	0.072	0.03
157	15/06/2009	6260	7.35	0.20	0.016	10.55	46.66	3.87	0.24	4.98	0.004	29.14	0.002	0.0002	3.80	3.67	0.32	32.88	20.02	37.38	0.06	-0.764	-1.69
231	15/06/2009	9550	7.40	0.05	0.106	14.27	78.50	3.02	0.36	7.21	0.010	48.33	< ql	0.0009	3.65	3.86	0.38	40.34	19.88	40.61	0.09	-0.003	-0.14
WWTP	01/07/2010	9550	8.30	0.90	0.123	5.28	67.50	10.75	1.59	5.90	2.520	70.12	0.604	0.3522	0.20	9.00	< ql	69.38	348.57	10.67	0.09	1.306	2.90
Piez 2	01/07/2010	3840	7.40	0.30	0.049	4.56	22.06	7.03	0.77	2.19	0.170	22.92	< ql	0.1739	1.81	3.73	0.26	23.11	42.55	16.99	0.05	0.063	-0.04
Piez 5	01/07/2010	502	7.85	0.22	<ql	0.76	2.01	1.72	0.41	0.19	0.090	2.26	< ql	0.0013	0.26	0.30	0.19	4.13	10.55	13.46	0.10	-0.993	-2.46
Piez 11	01/07/2010	4000	7.85	0.50	0.071	4.38	25.70	4.38	0.59	2.22	0.110	24.66	0.004	0.0011	1.75	3.86	0.45	25.56	47.27	21.03	0.03	-0.535	-1.21
60	01/07/2010	5240	7.65	0.16	0.046	10.89	34.95	3.54	0.29	4.78	0.040	20.23	0.003	0.0002	5.20	4.19	0.29	33.78	30.43	26.76	0.05	-0.338	-0.87
157	01/07/2010	6530	7.50	0.21	0.051	10.67	48.97	3.87	0.23	5.25	0.040	30.71	0.003	0.0002	3.53	3.58	0.33	29.33	30.25	29.21	0.05	-0.320	-0.8
231	01/07/2010	10000	7.45	0.17	0.160	14.51	81.27	3.87	0.41	7.61	0.030	51.89	0.004	0.0004	3.49	4.18	0.37	42.11	30.43	35.59	0.05	-0.140	-0.41
WWTP	25/07/2011	9840	8.45	1.32	0.09	5.70	77.80	9.92	1.58	6.68	2.400	74.95	1.256	0.0370	< ql	8.92	0.24	65.96	346.07	11.25	0.11	1.679	3.68
Piez 11	25/07/2011	4350	7.26	0.06	0.03	4.72	27.70	5.03	0.75	2.31	0.030	26.58	0.004	< ql	1.90	4.08	0.38	29.29	61.70	18.51	0.13	0.272	0.41
Piez 16	25/07/2011	1044	6.59	0.57	0.01	2.53	5.90	2.30	0.34	0.07	0.300	3.71	0.053	0.0007	0.88	0.27	0.07	6.64	2.77	19.89	0.11	-0.723	-2.81
30	25/07/2011	5110	6.97	0.03	0.05	10.69	36.73	2.92	0.29	4.73	0.002	19.49	0.007	< ql	4.72	4.16	0.29	39.84	22.66	33.98	0.11	0.081	-0.01
40	25/07/2011	7230	7.1	0.07	0.12	14.07	78.42	3.48	0.54	6.09	0.040	49.67	0.004	0.0028	3.29	5.01	0.20	131.56	29.97	45.19	0.10	0.331	0.49
162	25/07/2011	5990	6.96	0.04	0.06	11.16	47.28	3.49	0.17	4.58	0.010	26.79	< ql	0.0009	5.36	3.52	0.32	36.22	23.87	43.85	0.11	0.132	0.04
231	25/07/2011	8740	7.62	0.16	0.11	14.29	76.16	9.84	0.81	6.92	2.880	39.89	0.656	0.0011	< ql	3.37	0.50	39.57	27.38	42.66	0.11	1.270	2.40
Rain	11/2009	9.48																	19.35	22.88	0.12		

4.1 Major element concentrations

4.1.1 Groundwater quality

Generally speaking, the major element concentrations illustrate a strong variability of the water quality collected for this study in temporal and spatial terms. In wells, conductivity varied between 5,200 to 10,000 $\mu\text{S/cm}$. The highest conductivity was nonetheless recorded in piezometers 11 and 2 in 2009 (more than 12,000 $\mu\text{S/cm}$). Some samples had a notable low mineralization: (1) the 2010 Piez 5 sample (EC of 502 $\mu\text{S/cm}$); (2) the 2011 Piez 16 sample (EC of 1044 $\mu\text{S/cm}$). All pH were neutral, Piez 16 sample showing the most acid pH of the area (6.59). All major elements data are plotted in a Piper diagram representing the ion proportions (Fig. 3). Most of the control piezometers and some of the wells had essentially a sodium-chloride facies but some wells (60 and 162) evolved towards a calcium-sulfate facies. In wells, Cl amounts varied between 27 (Piez 11, 2011) to 81 mmol/L (Well 231, 2010, Table 1). In piezometers, it varied between 2 (Piez 5, 2010) to 139 mmol/L (Piez 11, 2009) and showed a decrease in 2011 compared to 2009 values (Table 1). The groundwater over the three years was generally enriched in calcium, sulfates and bicarbonates, compared with a simple mixing with seawater (Fig. 4). All the wells and some of the piezometers showed a Na deficiency most commonly combined with a K deficiency (see Fig1A in Supporting Information). Strontium was plotted in excess (points above the 1:1 line) versus Cl and Na+K.

The highest nitrate concentrations (seven times the potability norm of 0.7 $\mu\text{mol/L}$) were measured in wells 162 and 60, with low amounts of ammonium and dissolved manganese (Table 1 and Fig. 4). Thus (1) high nitrate (4.4–5.5 mmol/L) were combined with low chloride (<50 mmol/L) and low Mn (<0.06 mmol/L) contents, (2) medium nitrate (2.5–4.0 mmol/L) with increasing Cl contents (50–100 mmol/L) and intermediate Mn (0.01–0.03 mmol/L) concentrations in the wells in the middle of the plain and (3) low nitrates (< 1.5 mmol/L) with high chloride (150 mmol/L) and intermediate Mn contents (Fig 4j, k) (Cary et al., 2012a). Groundwater contamination in the region is due mainly to residual agricultural products like N-fertilizers. Manganese concentrations in the piezometers were higher than the amounts measured in wells (Table 1). The highest concentration of dissolved Mn was found in Well 231 associated to dissolved iron (0.3 $\mu\text{mol/L}$ in 2011), and was most certainly due to the sampling conditions.

It is notable that a high temporal variability was recorded in the same piezometer or well, e.g. in Piez 5 between 2009 and 2010.

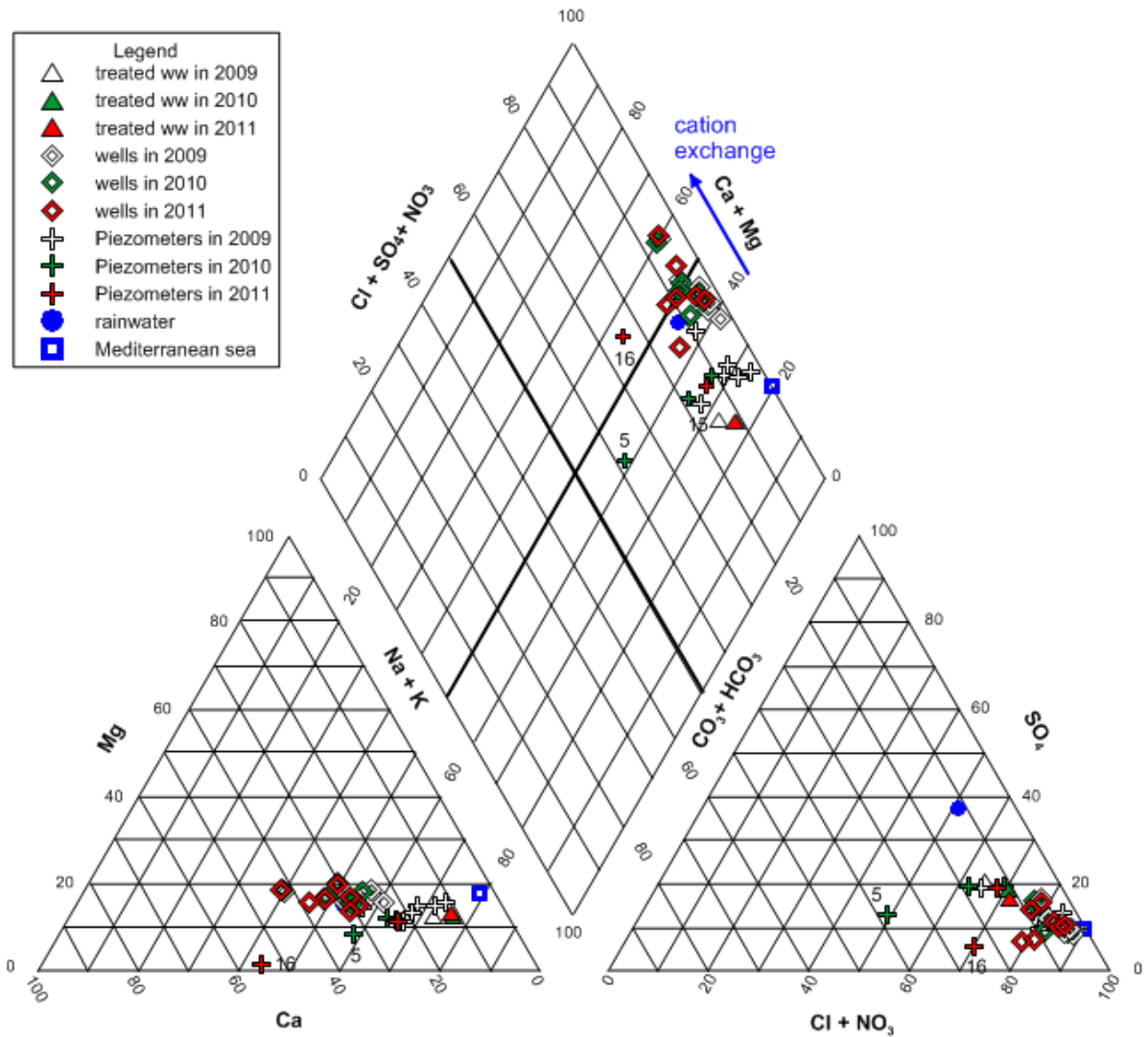


Figure 3: Piper diagram of the groundwaters and wastewaters monitored between 2009 and 2011.

4.1.2 Wastewater quality

The treated wastewater belonged to the sodium-chloride facies with a slightly alkaline pH (close to 8.3, Fig. 3). Conductivity over the three years varied at least between 5.2 and 9.8 mS/cm, and significant concentrations of Cl (respectively 33, 68 and 78 mmol/L) and Na (respectively 34, 70, 75 mmol/L) were measured in each year's wastewater (Table 1). The wastewater had high concentrations of Ca (3.7 to 5.7 mmol/L), K (1 to 1.6 mmol/L), SO_4 (5.2 to 9 mmol/L). The major elements showed no notable differences with those analyzed by El Ayni in 2008 (El Ayni et al., 2011). A yearly evolution can be expected depending on the different water uses and also on climatic variations.

4.2 Minor element concentrations

4.2.1 Groundwater quality

In wells, boron concentrations varied between 17.7 (Well 60, 2009) to 30 $\mu\text{mol/L}$ (Wells 157, 60, 231 in 2010) (Table 1). In piezometers, B amounts ranged from 2.7 $\mu\text{mol/L}$ in Piez 16 (2011) to 62.3 $\mu\text{mol/L}$ in Piez 2 (2009). The concentrations of trace elements as As, Cd, Co, Cr, Cu, F, Fe, Li, Ni, Pb and Zn in piezometers and wells are given in Table 1A in the supporting information. Piezometers contained higher concentrations of trace metals (e.g. Co, Ni, Cu, Pb) than the wells with variable metal concentrations in time and space. Except for Mn, all the piezometer metal concentrations were also higher than in the wastewater. Again, temporal variations were recorded in the same well or piezometer during the three years especially for Wells 231 and 157 between 2009 and 2010 or Piez 5 and 16. The bromide content varied between 0.01 (Piez 16) and 0.12 mmol/L (Wells 40 and 231). Points were plotted close to the seawater dilution line (Fig. 4h).

4.2.2 Wastewater quality

The wastewater had high concentrations of Al (0.9 to 3.3 $\mu\text{mol/L}$), B (64.4 to 346 $\mu\text{mol/L}$) and Sr (44 to 70 $\mu\text{mol/L}$) which may originate from the wastewater of local industrial activities. It also showed high concentrations of dissolved Mn (2.3 to 2.5 $\mu\text{mol/L}$) but low dissolved Fe, and very variable Li contents (from 8.7 to 41 $\mu\text{mol/L}$, Table 1A in Supporting Information). Nitrate concentrations were low between the quantification limit and 0.2 mmol/L meaning that, at least on the sampling dates, the treatment plant was efficient for nitrate removal. The three ammonia values were especially high (1.13, 0.6 and 1.26 mmol/L) exceeding previous high values (Chemingui et al., 2011). Nitrite concentrations were usually high, reaching 0.35 mmol/L except in 2011 (0.037 mmol/L).

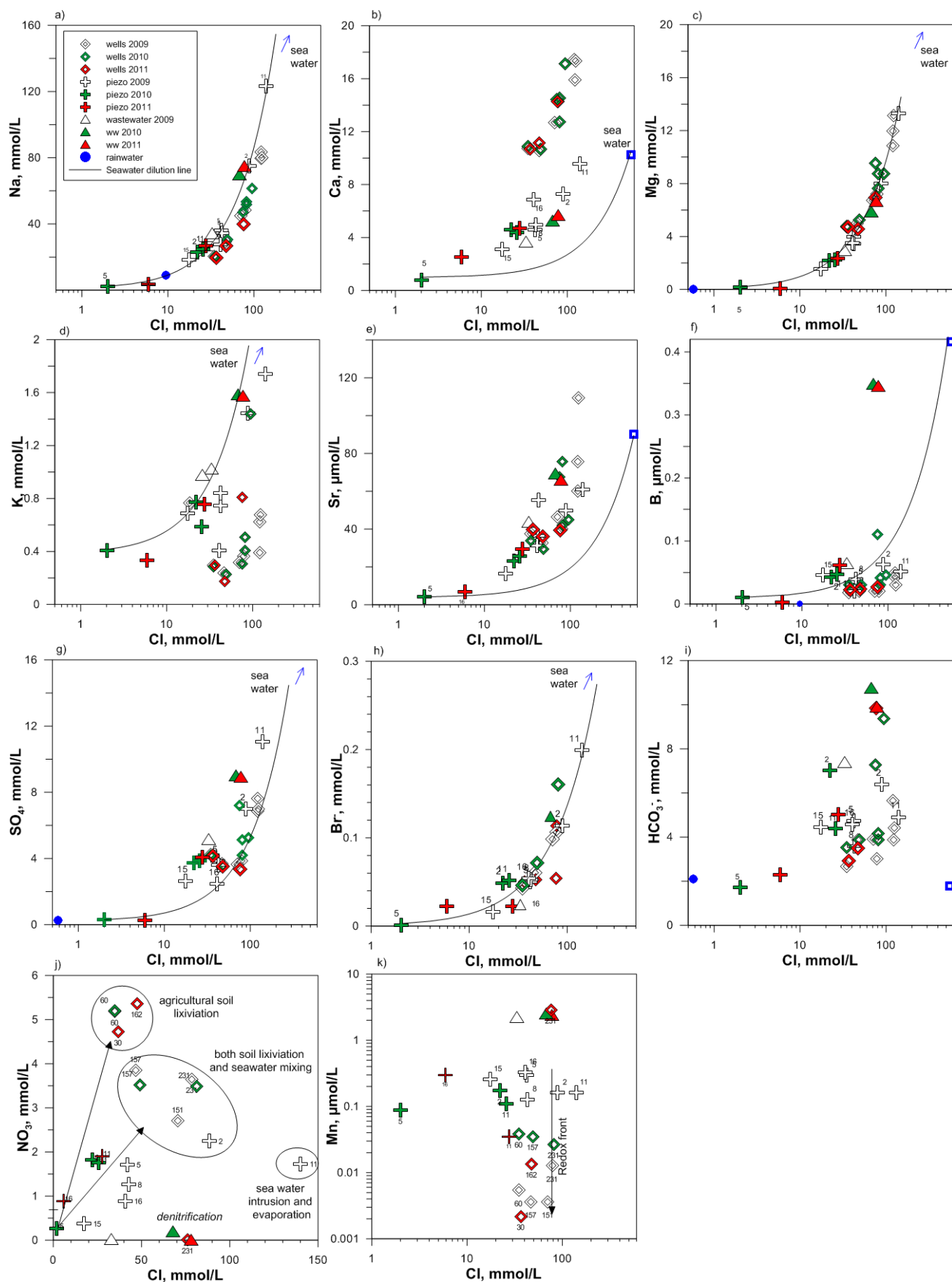


Figure 4: Element diagrams for concentrations measured in piezometers, wells and treated wastewaters in 2009, 2010 and 2011.

4.3 Boron concentrations and isotopic composition

4.3.1 Groundwater

Actively pumped wells of the Plio-Quaternary groundwaters (60, 151, 157 and 231) had $\delta^{11}\text{B}$ varying between 26.8‰ and 42.7‰ associated with boron levels varying between 18 and 30 $\mu\text{mol/L}$ (Table 1).

Spectacular shifts of $\delta^{11}\text{B}$ were measured in the 2009-2010 composition of Piez 2 and 11 from a high of 30-45‰ to 17-21‰ in 2010-2011. The B isotopic composition in Piez 11 evolved after a maximum of 7 months of recharge and then remained nearly stable between 2010 and 2011.

The composition of Piez 5 varied in time. Although its boron isotopic signature is high ($\delta^{11}\text{B}$ of 33.4‰ and B concentration of 34.4 ng/L) in 2009, it decreased down to $\delta^{11}\text{B}$ of 13.5‰ and B concentration of 10.6 $\mu\text{mol/L}$ in 2010. The fresh groundwater found in Piez 16 in 2011 had a $\delta^{11}\text{B}$ of 19.9‰. Piez 15 in 2009 had a $\delta^{11}\text{B}$ of 16‰ with a low conductivity of 2.9 mS/cm .

4.3.2 Treated wastewater

The $\delta^{11}\text{B}$ signature of treated wastewater varied between 10.7‰ and 13.9‰ with high boron concentrations ranging from 65 to 348 $\mu\text{mol/L}$.

4.4 Carbamazepine

4.4.1 Groundwater

The CBZ concentrations in groundwater varied over a very large range from 20.4 in Piez 5 (2010) to 910 ng/L (Piez 2 (2011)) (Table 2), some piezometers being below the quantification limit. Except for Well 19 (397 ng/L CBZ), the other wells did not show CBZ in 2010 nor 2011. Important increases were recorded in Piezometers 2 and 11 with time, e.g. respectively from 486 and 400 ng/L in 2010 to 910 and 593 ng/L in 2011, along with a high value measured in a new piezometer close to Piez 11 (11', CBZ of 519 ng/L).

4.4.2 Treated wastewater quality

Bi-daily sampling over four consecutive days to evaluate the carbamazepine concentrations pointed out variations between 249 and 422 ng/L with a mean value reaching 328 ng/L ($n=8$) and a standard deviation of 61 ng/L (Table 2). Data showed a large short term variation reflecting daily inputs variations from domestic households and industries which are mainly of food, textile, dairy, and paper. This means that a greatest variation range of CBZ content could be expected within a full year.

5 Discussion

5.1 Temporal chemical and isotopic variations

The geochemical data, whether concentration or B isotopic composition, exhibit large variability between the three years; it is generally more pronounced for piezometer than for wells samples. The boron isotopic compositions significantly shifted back-and-forth (e.g. see Well 231, Table 1). The $\delta^{11}\text{B}$ shifts with time in the piezometers (2, 11, 15) under the influence of the treated wastewater recharge helps demonstrate the high system reactivity, especially through equilibrium processes as sorption reactions. These major variations between fresh and brackish facies are interpreted as due to the spatial displacement and temporal mixing of Plio-Quaternary groundwater with fresh groundwater and recharge water under various hydrodynamic constraints such as the infiltrated recharge volume, withdrawals, and meteoric recharge. The superimposition of a 'recharge front' due to the new 'treated wastewater' component modified the previous transitional states by adding two new constraints, i.e. the entry of a new boron and CBZ source and the development of reductive conditions with the intrusion of high amounts of organic matter compared to the groundwater content, as measured by El Ayni et al. (2008).

5.2 Main processes

5.2.1 Mixings of water bodies

In the Na vs. Cl diagram (Fig. 4a), all piezometer samples, especially 2 and 11 (2009), and the treated wastewater were plotted on the seawater dilution line showing simple mixing with recharge water. The fresh water point used to calculate the seawater dilution line is Piez 5 (2010).

The Plio-Quaternary groundwater had various degrees of salinization (see details in supporting information and Table 2A). No sample showed a simple mixing with seawater (Fig. 4). Piezometers 5 in 2010 and 16 in 2011 presented a different behavior indicating a local fresh-water contribution. Their very low calcium, sulfate and strontium concentrations indicated low water rock interactions and more likely equilibrium with sand, sandstone or rainwater than with the Plio-Quaternary carbonates (Cary et al., 2012a).

5.2.2 Mixing and water-rock interactions

The groundwater over the three years of study was generally enriched in calcium, sulfates, bicarbonates and strontium, compared with a simple mixing with seawater (Fig. 4). It showed almost no enrichment in magnesium and depletion in sodium and potassium. Na and K depletion along with Ca and Sr enrichment are in agreement with the cation exchange process (detailed in the Supporting Information) which were previously described (Ben Hamouda et al., 2011; Cary et al., 2012 a,b; Kouzana et al., 2009; Lerouge et al., 2010;). Saturation indexes were calculated and are shown for calcite and dolomite on Table 1. Supersaturation with carbonates due to cation exchange may hide other processes such as calcite dissolution, which can contribute to an increase in Ca, Mg, Sr, and also to an increase in B mobility (Goldberg and Forster, 1991). Although seawater is the main sulfate contributor, gypsum saturation indexes are in favor of its dissolution, which would thus add both Ca and SO_4 to the solution. Although an increase of Mg^{2+} in solution has been observed in several clay-bearing coastal aquifers affected by seawater intrusion (Bianchini et al., 2005; Vengosh et al., 2002), The absence of Mg enrichment can be linked to its sorption on exchanger phases like Na^+ and K^+ and compensates Ca^{2+} and Sr (Goren et al., 2011; Griffioen, 1993). Although boron is supplied by seawater, most of well samples were plotted under the seawater dilution line (Fig. 4f). The main suggested mechanism is B adsorption on clay, metal (hydr)oxides, organic matter and even carbonates (Goldberg and Forster, 1991; Majidi et al., 2010). Nevertheless, the rather low B concentrations in wells can also be explained by a dilution with Miocene fresh groundwaters due to natural drainance as already suggested by Ben Hamouda et al., (2011) and also to all the human strategies to enhance recharge of the Plio-Quaternary aquifer with fresh Miocene groundwaters through dams, surface irrigation network and direct recharge in wells (BURGEAP and CRDA, 2004).

5.3 Origin of water masses

The boron isotopic composition versus the molar ratio Cl/B are given in Figure 5 along with the $\delta^{11}\text{B}$ versus 1/B. The Plio-Quaternary groundwater pole is constituted by wells 60, 151, 157 and 231, with $\delta^{11}\text{B}$ varying between 26.8‰ and 45.2‰ and associated with low boron levels varying between 17.73 and 30.43 $\mu\text{mol/L}$. Although our sampling strategy was orientated towards actively pumped wells which salinity was lower enough to still allow irrigation, the boron and chloride contents of the Plio-Quaternary group (respectively 20 to 30 $\mu\text{mol/L}$ and 47 to 80 mmol/L) are nevertheless lower than can be expected in such a salinized environment. This is consistent with a meteoric recharge which was confirmed with stable isotopes (Ben Hamouda et al.,

2011; Ben Moussa et al., 2009). It can also result from mixing with lowly mineralized groundwaters like in Piez 16 (2011) with a $\delta^{11}\text{B}$ between 16‰ and 20‰ with very low B contents (3 $\mu\text{mol/L}$). These fresh groundwaters could represent a deep Miocene pole. To our knowledge, the origin of such fresh groundwaters in this very limited area is not clear but could be linked to the presence of faults affecting miocene formations and favoring mixings (Fig. 1c). Electric diagraphs showed a 2 m fresh groundwater level at the top of the salinized Plio-Quaternary groundwater (BURGEAP and CRDA, 2004). The spatial influence of this fresh groundwater body varied in time as showed with the evolution of composition of groundwater in Piez 5, which is plotted on the Plio-Quaternary pole in 2009 and on a mixing curve between local treated wastewater and fresh ground water in 2010 (an equivalent to the Piez 16 in 2011). It corresponds to a mixing of 10 % of treated wastewater and fresh water.

High $\delta^{11}\text{B}$ values ($> 39\text{‰}$) like in Piez 11 in 2009 or Well 40 in 2011 (respectively 51.2 and 45.2 ‰) could result from infiltration of seawater into the aquifer leading to B adsorption and decreasing B contents, and define the most salinized part of the Plio-Quaternary groundwater. The marine contamination has recently been confirmed with stable isotopes in the Korba-Mida aquifer (Ben Hamouda et al., 2011) and in the southern border Hammamet–Nabeul shallow aquifer (Ben Moussa et al., 2009). The Plio-Quaternary groundwater had $\delta^{11}\text{B}$ similar to those measured by Vengosh et al. (1994) in the coastal plain of Israel.

Nevertheless, some samples show a higher Cl/B ratio (Wells 151 and 231 in 2009) with $\delta^{11}\text{B}$ close to 40 ‰. Here, salinization could originate from mixing with an entrapped and fossil groundwater which evaporated and evolved, leading to increasing Cl/B ratios (Fig. 5). This entrapped groundwater could be also found in the Miocene aquifer which contains clays and marls that can adsorb boron and cause B diminution and $\delta^{11}\text{B}$ increase. This hypothesis is supported by the evaporation identified in some groundwaters samples again with stable isotopes by Ben Moussa et al. (2009).

5.4 Groundwater contamination by wastewater

The isotopic signature of anthropogenic boron issued from treated wastewaters used for artificial recharge varied between 10.7‰ and 13.9‰ with high boron concentrations ranging from 65 to 348 $\mu\text{mol/L}$ and associated with low Cl/B ratios. These recorded values are within the range of reported values (Kloppmann et al., 2009; Vengosh et al., 1994). Mixing of the treated wastewater with the Plio-Quaternary groundwater is represented by the 2009-2011 composition of Piez 2 and 11. The B isotopic composition in Piez 2 evolved towards a recharge signature after a maximum of 7 months of recharge. The hydrodynamic survey showed

that the treated wastewater reached Piez 11 (150 m away) one month after its infiltration into the basins. According to the mixing curves, a maximum of 40-60% of the treated wastewater was mixed in the groundwater of these piezometers. The 2009 $\delta^{11}\text{B}$ signature recorded in Piez 15 indicated a high degree of mixing with treated wastewater. Piez 15 being located in the wastewater treatment plant, this fact is more likely linked to losses from the plant, meaning that groundwater was surely already impacted by wastewater infiltration before the implementation of artificial recharge.

Boron signatures vs. carbamazepine concentrations are presented in Fig. 5c. High contents of CBZ were measured in groundwaters thus indicating clear contamination by recharge waters. In piezometers 2 and 11 located very close to the recharge basins, the CBZ concentrations increased by respectively 87% and 48% between 2010 and 2011. The high content of CBZ in Well 19 (397 ng/L) seems to indicate again wastewater infiltration towards groundwater from the treatment plant.

Notable very low contents were measured in Piez 5 in 2010 (20.4 ng/L) and in Piez 4 in 2011 (24 ng/L), and can indicate a high dilution rate of the treated wastewater by the deep Miocene fresh groundwater. This means that the fresh water flows are important and their refreshing role could be more considered in this area. The presence of high CBZ contents in both Piez 10 and Well 19 (260 and 400 ng/L) raises again the question of losses from the treatment plant rather than infiltration from the recharge site. The hydrodynamic context is favorable to losses knowing that in 2011, the 0 isopiestic line frequently traversed the plant, and negative piezometric levels were found in the area (Gaaloul et al., 2012).

The other CBZ values were lower than those measured in Shafdan (900 to 1400 ng/L in the recharged treated wastewater), which is to be expected considering that Shafdan receives municipal wastewater from the greater Tel Aviv region (Arye et al., 2011). The CBZ values are up to 6 times those reported by Fenet et al. (2012) in piezometers in the vicinity of an artificial aquifer recharge site and in wells after irrigation of agricultural soils with treated wastewater at Nabeul, underlain by the same coastal aquifer in similar geological conditions 20 km south of Korba (see Fig. 1a). The geological condition are thus in favor of a high transfer rate of CBZ towards the groundwater due to very low adsorption in link with a very low organic matter content as shown by Fenet et al. (2012). Nevertheless, the high CBZ values of our study area do not correspond to what could be expected with a mixing of 40-60 % of treated wastewaters with an average value of 328 ng/L, e.g. CBZ concentrations between 130 to 200 ng/L of CBZ. First of all, the increase of CBZ amounts in groundwater can be linked to high temporal concentration changes in the injected treated wastewater as schematized in Fig 5c. This was already observed by Clara et al. (2004) who showed that CBZ content varied between 400 and 2500 ng/L during 4 different campaigns in two years, and by Bekele et al. (2011) during a 39-month managed

aquifer recharge; this can also be suggested by the variability of the CBZ content during the bi-daily survey on four consecutive days (Table 2). Secondly CBZ is expected to sorb on DOM which is co-introduced in the aquifer during recharge (Maoz and Chefetz, 2010). This means that CBZ mobility and transfer are controlled by all processes that affect effluent- and sludge-derived DOM during its transfer from the infiltration basin towards the unsaturated and the saturated zones of the aquifer, and also sludge sedimentation, organic matter mineralization in the basin sludge during anaerobic or aerobic conditions, etc. According to Chefetz et al. (2008), CBZ is a slow-mobile compound in SOM-rich soil layers but its mobility is significantly increased when introduced into SOM-poor soils. Nevertheless, more studies are still needed to better understand the impact of DOM degradation during its transfer and the consequences on CBZ mobility and content in groundwater under the context of artificial recharge. A high frequency monitoring of CBZ content in effluents and groundwater is therefore needed.

Finally, to have a more complete overview of CBZ contamination, the role of CBZ metabolites must be taken into account. They have been measured in wastewater at a higher concentration than the parent compound (Hummel et al., 2006) or in wastewater treated wastewaters (Leclercq et al., 2009) and can be expected in the groundwaters in our site.

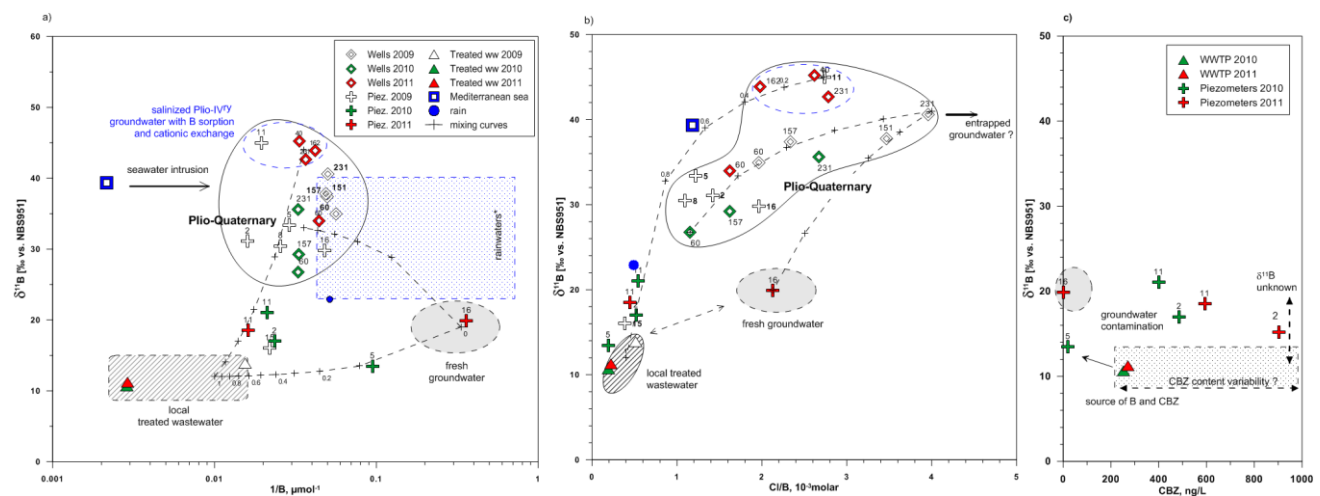


Figure 5: a) $\delta^{11}\text{B}$ versus $1/B$ in samples from the wells, piezometers, and wastewater recharge plant during the three years. b) Boron isotopic composition versus the 10^{-3} molar ratio Cl/B , (c) Boron isotopic signatures versus carbamazepine concentrations for piezometer samples in 2010 and 2011. The $\delta^{11}\text{B}$ of Piez 2 in 2011 was not measured. Error bars are within the points. The boron isotopic compositions and rainwater concentrations* are taken from Millot et al. (2010). All mixing curves were calculated using binary mixing lines according to Faure (Faure, 1986).

5.5 Salinity and redox fronts in the studied area

The conceptual pattern of Figure 6 plots the geographic extension of the area concerned by high $\delta^{11}\text{B}$ and cation exchange and is in good agreement with the Taffeloun salinity axis where the groundwater is directly recharged by surface waters inputs in wells. The increasing salinization of the groundwater combined with agricultural practices is gradually impacting the groundwater quality. The superimposition of a 'recharge front' due to the new 'treated wastewater' component modified the previous transitional states away from equilibrium by adding a new constraint, i.e. the development of reductive conditions with the intrusion of high amounts of organic matter and the entry of a new boron and CBZ source as represented in Figure 6. Although the natural amounts of metals in the aquifer is not known, pollutant metals issued from human activities were injected into the aquifer and the oxido-reductive conditions enhanced their mobility. The well documented salinity front, which is not geographically homogeneous due to the geological and hydrodynamic conditions, generates mixing with groundwater of the order of less than 20% of the seawater fraction (Table 2A of the supplementary information), which is coherent with the previously cited studies.

The notable evolution of the boron isotopic signature in the wells between 2009 and 2011 was probably due to the irregular progression of the seawater intrusion affected by natural recharge, withdrawals, and irrigation and mixings with Miocene groundwaters. Salinity at the recharge site generally decreased from 10 g/L in 2004 (BURGEAP and CRDA, 2004) to 2-3 g/L in 2011; here attention must be paid to the role of the fresh groundwater body whose refreshing effect must not be confounded with that of the recharge waters. It is spatially and temporally displaced, possibly under the piston effect due to the infiltration of 6,000 to 37,000 m³ of wastewater per month.

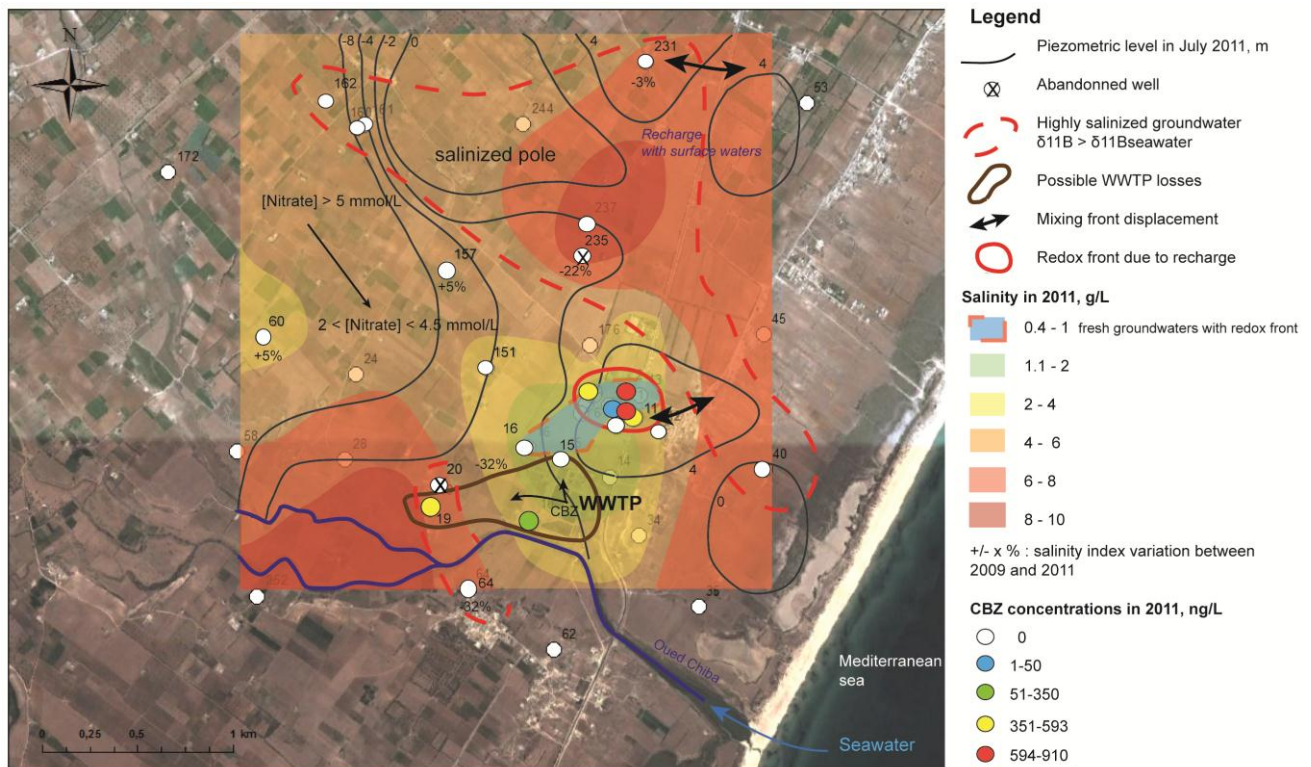


Figure 6: Conceptual pattern of chemical fronts and mixing areas with the freshwater body in the vicinity of the Korba recharge site in the Korba plain. Salinity index variations were calculated from the ratio between the 2011 and 2009 references, except for Well 157 (2010/2009). The geographic extension of the area concerned by high $\delta^{11}\text{B}$ and cation exchange is in good agreement with the Taffeloun salinity axis where the groundwater is directly recharged by surface waters inputs in wells.

6. Conclusion

The combination of boron isotopic signatures with boron and carbamazepine contents proved to be a useful tool to assess sources and mixing of sewage effluents in groundwaters and to study the combined effects of abstraction, natural recharge, seawater intrusion, and artificial recharge, on groundwater dynamics. It is particularly adapted to study the mixing interfaces between the various water poles in a dynamic system. This combination can also be useful when effluent and groundwaters have similar boron isotopic signatures.

Concerning the MAR objectives, the impact of the artificial recharge is limited as a refresher when considering its brackish facies, and is clearly polluting in view of the CBZ concentrations. Wastewater treatments need to be greatly improved before recharge to prevent further degradation of groundwater quality. The dynamics of the studied system was pointed out by the spatial and temporal variability of element contents, including B

isotopic signature, revealing the complexity of the groundwater contamination by salinization and anthropogenic activities. The system is highly vulnerable and permanently disturbed by the different temporal dynamics of continuous processes such as cation exchange, and by threshold processes linked to oxidation-reduction conditions which are enhanced by the intrusion of treated wastewaters and seawater.

The two tracers can be usefully associated for integrated water resource planning and for building a hydrodynamic model of wastewater flushing in an aquifer. Yet, more studies about CBZ monitoring at high frequency in treatment plants and in groundwater and about the impact of DOM degradation on CBZ mobility are needed to better evaluate CBZ transfer towards the aquifer.

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