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## The hydrogeochemistry of a heavily used aquifer in the Mexican wine-producing Guadalupe Valley, Baja California

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**Abstract** The Guadalupe Valley aquifer is the only water source for one of the most important wine industries in Mexico, and also the main public water supply for the nearby city of Ensenada. This groundwater is monitored for major ion, N-NO<sub>3</sub>, P-PO<sub>4</sub>, Fe, As, Se, Mo, Cd, Cu, Pb, Zn and Sb concentrations, as well as TDS, pH, dissolved oxygen and temperature. High concentrations of N-NO<sub>3</sub> (26 mg l<sup>-1</sup>), Se (70 µg l<sup>-1</sup>), Mo (18 µg l<sup>-1</sup>) and Cu (4.3 µg l<sup>-1</sup>) suggest that groundwater is being polluted by the use of fertilizers only in the western section of the aquifer, known as El Porvenir graben. Unlike the sites located near the main recharge area to the East of the aquifer, the water in El Porvenir graben has low tritium concentrations (<1.9 TU), indicating a pre-modern age, and thus longer water residence time. No significant variations in water quality (generally <10%) were detected throughout 2001–2002 in the aquifer, suggesting that reduced rainfall and recharge

during this dry period did not significantly affect water quality. However, the wells nearest to the main recharge area in the Eastern aquifer show a slight but constant increase in TDS with time, probably as a result of the high (~200 L S<sup>-1</sup>) uninterrupted extraction of water at this specific recharge site. Relatively high As concentrations for the aquifer (10.5 µg l<sup>-1</sup>) are only found near the northern limit of the basin associated with a geological fault.

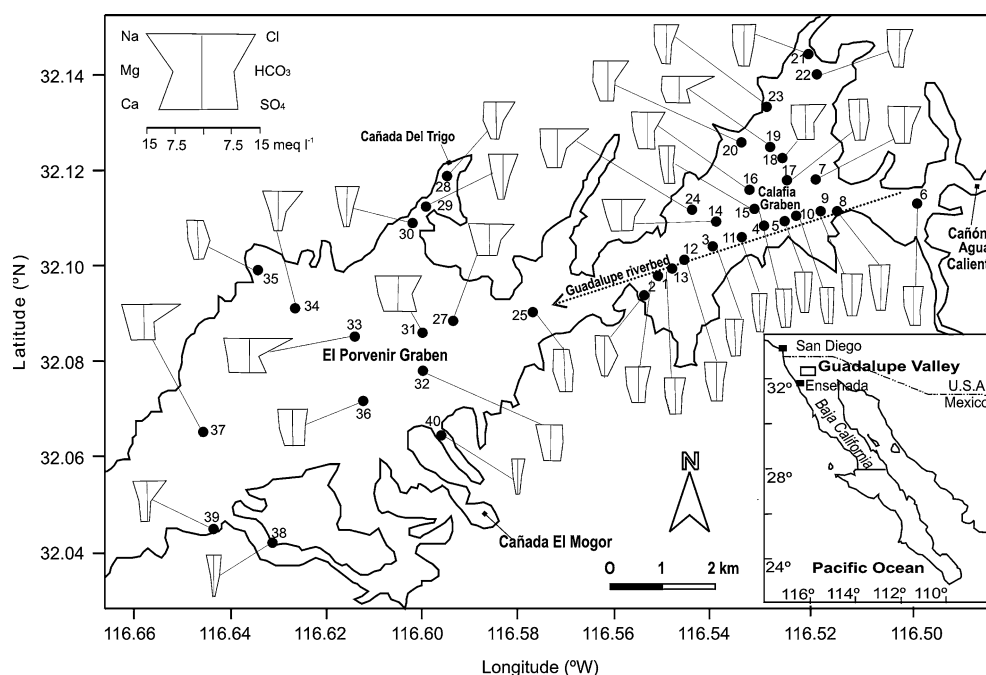
**Keywords** Mexico · Baja California · Guadalupe Valley · Groundwater · Phosphate · Nitrate · Fertilizers

### Introduction

The Guadalupe valley (Valle de Guadalupe) is located ~30 km NE of the coastal city of Ensenada in Baja California, NW Mexico (Fig. 1). By 1998, about 418 active wells were registered with depths ranging from 3 to 45 m below surface (SRH 1977; CNA 1999). At least five large and several small-scale Mexican wineries depend on groundwater extraction from the Guadalupe

aquifer to produce ~90% of nationwide table wines. In addition to agriculture, ca. 9 Mm<sup>3</sup> a<sup>-1</sup> of water is extracted to supply the city of Ensenada and towns in the valley (CNA 1998). The aquifer is composed of three main lithologic sections of variable thickness: (a) highly permeable gravel, sand and silt with some clay lenses and igneous rock boulders, (b) semi-permeable sandstones and conglomerates and (c) a granodiorite impermeable basement (SRH 1977). The main ground-

**Fig. 1** Study area, sample location and Stiff diagrams indicating water composition in 37 wells from the Guadalupe aquifer in September 2001



water reservoirs in the aquifer are thought to be formed by two tectonic grabens, Calafia and El Porvenir (Fig. 1), which have depths to basement of  $\sim 350$  and 100 m, respectively (CNA 1999). Although extension and geometry are poorly studied, it is known that the grabens are delimited by a series of structural faults, which are thought to serve as additional recharge sources. However, the hydraulic gradients (which are probably irregular) and the water fluxes have not been studied so far (Andrade-Barbilla 1997).

The total storage volume of the Guadalupe aquifer is  $\sim 218 \text{ Mm}^3$  (Andrade Barbilla 1997; CNA 1999). Transmission coefficients average  $> 1 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}$  with the main flux running along the Guadalupe riverbed toward the west (Fig. 1). Total water discharge between 1990 and 1999 was estimated to be  $23.8 \text{ Mm}^3$ . Despite the low rainfall in the region (averaging 278 mm during 1963–2003), the recharge during the 1990–1998 period is reported to be  $30.6 \text{ Mm}^3$  (an unusually wet period), compared to  $18.0 \text{ Mm}^3$  during a drier period from 1973 to 1977 (CNA 1999), suggesting a slightly negative hydrological balance for the 1970s. Data available for September 1996–August 1997 also indicate a slightly negative balance between recharge and discharge of  $-0.908 \text{ Mm}^3$  (Andrade-Barbilla 1997). Despite the lack of more precise and/or recent information, the water balance has been significantly altered after 1998 in response to an extended drought in recent years and continuous water extraction and sand mining from the aquifer.

The years prior to the present study (1999–2001) were unusually dry compared with the 1948–2002 historical rain average of  $250 \text{ mm a}^{-1}$  (Ensenada meteorological station). Rainfall averaged  $131 \text{ mm a}^{-1}$  in 1999,

$158 \text{ mm a}^{-1}$  in 2000,  $284 \text{ mm a}^{-1}$  in 2001 and  $125 \text{ mm a}^{-1}$  in 2002. Simultaneously, water demand has rapidly increased due to the growth in urban population, which increased from 315,289 in 1995 to 370,730 in 2000 in Ensenada County.

Overall knowledge of the hydrogeology and geochemistry of the aquifers in this region is limited. The only scientific paper published on the hydrogeology of the area deals with the nearby Ojos Negros aquifer (upstream of Guadalupe) and not directly with the Guadalupe aquifer (Ponce et al. 1999). The most recent known hydrogeochemical data for the Guadalupe aquifer date back to 1990 and tracks only major ions. The geochemical information available for this aquifer suggests a significant variation in the regional distribution of major ion concentrations and distribution patterns. This compositional variation, in addition to the high recharge rate from known and unknown water sources in a highly fractured terrain (Andrade-Barbilla 1997), suggest that the aquifer is a complex hydrological system that needs to be studied to understand its hydrogeological response and evolution. Geochemical results of a 2001–2002 hydrogeochemical survey from 37 wells from the Guadalupe Valley are presented here. The results are discussed in terms of the regional evolution of water quality and the probable natural and/or anthropogenic causes for compositional variability.

## Materials and methods

Water samples were collected from 36 active wells and one spring in September 2001. In April and November

2002, 24 wells were re-sampled during follow-up surveys. Immediately after collection, water was analysed in the field for alkalinity (Clesceri et al. 1998). Total dissolved solids (TDS), dissolved oxygen (DO), pH and temperature were measured in the field with an YSI 6600 probe. The samples were filtered through 0.45  $\mu\text{m}$  cellulose nitrate, acidified with trace-metal grade  $\text{HNO}_3$ , and stored at 4°C in cleaned polyethylene bottles prior to metal, Se and As analyses (Walsh 1997). Samples for nutrient analyses were filtered through GF/F pre-combusted filters and kept frozen. The concentrations of Ca, Mg, Na, K and Fe were determined with a Thermo Jarell Ash Iris ICP-AES, As with a furnace Varian SpectraAA 880 AAS, and trace elements (Cd, Cu, Mn, Pb, Zn, Se, and Sb) with a VG Elemental PlasmaQuad3 ICPMS. Cl was analysed by the argentometric method using a HACH 2010 spectrophotometer, and  $\text{SO}_4$  was analysed using the turbidimetric method (Clesceri et al. 1998). Nitrate (expressed as  $\text{N-NO}_3$ ) and phosphate (expressed as  $\text{P-PO}_4$ ) were analysed with a Skalar San Plus automated nutrient analyzer. Analyses of prepared and certified water standards and replicates for quality control suggest bias and precisions better than 8% for all elements studied. The charge balance between major anions and cations is better than  $\pm 5\%$ . Tritium analyses in two selected samples were carried out with a liquid scintillation counter at Geochron laboratories, USA, with a 1.9 TU detection limit.

## Results and discussion

### Total dissolved solids (TDS)

On a regional scale, TDS concentrations in the aquifer range from 0.41 to 2.72  $\text{g l}^{-1}$  (Table 1; Fig. 2). TDS concentrations are highest in the western region of the aquifer (in El Porvenir graben) and in the northern section of the Calafia graben region to the northeast (2.3–2.7  $\text{g l}^{-1}$ ), and lower within the area adjacent to the Cañon Agua Caliente to the west, where 11 wells for urban supply are operated by the State Public Services Commission (CESPE). The water in these wells is relatively cold compared with most of the wells in the aquifer ( $T < 19^\circ\text{C}$ ),  $\text{pH} > 7.2$  and has low TDS values (0.5–1.0  $\text{g l}^{-1}$ ). Low TDS values are also found in water from the southwest aquifer near Cañon El Mogor (samples 38, 39, and 40), suggesting a relatively unpolluted water source to the aquifer, probably from local surface runoff and/or through multiple faulting in this area. A third area with low TDS concentrations was found in a small sub-basin, Cañada el Trigo, north of the Guadalupe basin (samples 28, 29 and 30). Reports for 1977 when TDS concentrations in the aquifer were 0.4–3.0  $\text{g l}^{-1}$  (Table 2), suggest that TDS have not increased historically overall and that the regional distri-

bution of TDS values has been variable throughout the aquifer (SRH 1977). More recent and less detailed results for 1990 report TDS concentrations  $\sim 5 \text{ g l}^{-1}$  in El Porvenir and as low as 0.4  $\text{g l}^{-1}$  where the Cañon Agua Caliente natural recharge site is located (CNA 1991; INEGI 1995). In 2001–2002, TDS concentrations in these same sites were  $< 3.0 \text{ g l}^{-1}$  and  $< 1.0 \text{ g l}^{-1}$  respectively, suggesting that fluctuations in recharge and discharge rates have not significantly affected overall TDS concentrations over the last 25 years. Groundwater near the Cañon Agua Caliente main recharge site is pumped from several constantly operated wells. Throughout the first 4 km down gradient after water is recharged into the aquifer during rain periods, TDS concentrations remain constantly below 0.7  $\text{g l}^{-1}$  (September 2001). Further west, however, at  $\sim 5 \text{ km}$  from the recharge site, water quality decreases rapidly, reaching the limit of 1.0  $\text{g l}^{-1}$  for TDS established by the Mexican Government (Diario Oficial de la Federación 2000) as the maximum allowed level for water for human use and consumption (Fig. 2). In the follow-up surveys from April and November 2002, TDS concentrations increased with time in these wells, especially in those closer to the recharge site (8, 9, and 10 in Fig. 3).

On a regional scale, no significant changes in water quality were seen when comparing results for 25 wells over a 1 year period (September 2001, April 2002 and November 2002, Table 1). Increases of up to 10% compared to 2001 are seen in samples with both high and low TDS concentrations, and no clear correlation with well location was seen. Only sample 32 shows an increase in TDS  $> 10\%$ . However, it is suggested that the intensive mining of sand from the Guadalupe riverbed is causing increased evaporation from the exposed saturated zone and consequently a decrease in water quality at specific sites (Badán et al. 2006).

### Major ion geochemistry and water residence times

The concentrations of major ions in groundwater from the Guadalupe aquifer are shown in Table 1. The highest concentrations of major ions (including  $\text{N-NO}_3$ ) are found in the Porvenir graben, where also the highest TDS concentrations are found. The concentrations of major ions in water from wells at or near El Porvenir are above the maximum concentrations accepted by the Mexican norms and US EPA limits for drinking water (Table 1, 2). Nitrate concentrations at these enriched sites (especially samples 33, 36 and 37) are as high as those reported by Daesslé et al. (2005) for the nearby Maneadero coastal aquifer, where the enrichment of this element has been associated with fertilizer use.

The groundwater in the Guadalupe aquifer can be classified into two main compositional types: (a) those waters having high TDS concentrations ( $> 1 \text{ g l}^{-1}$ ) and a

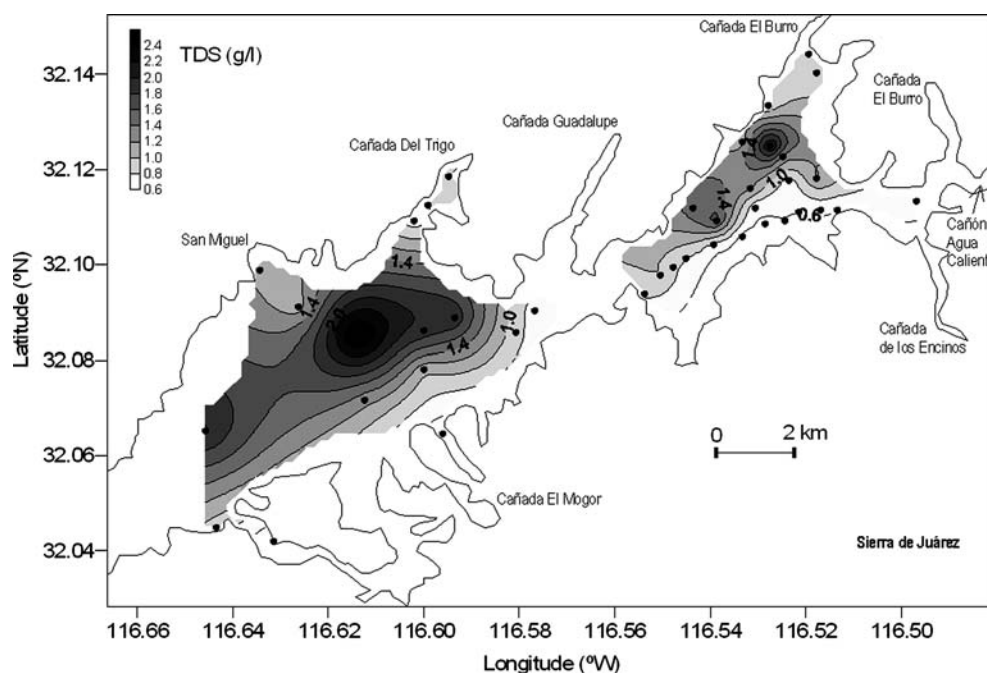
**Table 1** Groundwater composition in the Guadalupe Valley in September 2001

ID	Latitude (°N)	Longitude (°W)	T	pH	TDS (g l <sup>-1</sup> )		Ca (mg l <sup>-1</sup> )	Mg (mg l <sup>-1</sup> )	Na (mg l <sup>-1</sup> )	K (mg l <sup>-1</sup> )	Cl (mg l <sup>-1</sup> )	SO <sub>4</sub> (mg l <sup>-1</sup> )	HCO <sub>3</sub> (mg l <sup>-1</sup> )	N-NO <sub>3</sub> (mg l <sup>-1</sup> )	P-PO <sub>4</sub> (mg l <sup>-1</sup> )	Fe (µg l <sup>-1</sup> )	As (µg l <sup>-1</sup> )	
					TDS	Ca												
Sep. 01																		
Apr. 02																		
Nov. 02																		
<sup>a1</sup> 32.09772	116.55054	19.4	7.2	1.00	1.15	1.01	3.4	132	44	172	2.5	246	184	279	3.9	0.06	4.1	0.51
2 32.09384	116.55376	18.7	7.2	0.83	0.78	0.74	1.8	115	35	146	1.9			324	2.4	0.15	6.2	
<sup>a3</sup> 32.10411	116.53925	17.6	7.3	0.70	0.81	0.87	5.2	94	28	122	2.0	163	120	196	3.2	0.30	3.1	0.44
<sup>a4</sup> 32.10845	116.52849	17.1	7.3	0.58	0.64	0.65	6.1	78	22	107	1.7	120	138	238		0.16	4.2	0.19
5 32.10913	116.52446	17.3	7.3	0.60			4.9	81	21	119	2.0	133	93	192		0.12	4.2	0.28
<sup>a6</sup> 32.11324	116.49677	19.5	7.6	0.68	0.76	0.83	9.0	92	26	126	3.3	171	146	220		0.07	2.5	0.63
7 32.11804	116.51774	21.0	7.0	1.22	1.26	0.97	5.5	159	54	183	4.0	332	165	312	5.5	0.07	4.5	
8 32.11142	116.51344	17.9	7.2	0.59	0.73		5.1	75	21	113	2.5	99	206			0.17	7.4	
<sup>a9</sup> 32.11142	116.51694	17.6	7.4	0.67	0.77	0.81	7.9	91	26	117	3.0	155	111	255			3.7	0.40
10 32.11096	116.52151	17.5	7.2	0.60	0.78	0.85	4.8	84	23	109	2.8	132	116	181		0.15	4.4	0.83
11 32.10594	116.53333	18.0	7.3	0.54		0.65	6.2	71	20	99	1.5	109	91	175	0.5	0.10	6.2	0.07
<sup>a12</sup> 32.10137	116.54516	18.5	7.2	0.81	0.85	0.87	5.0	111	32	137	2.1	186	139	206	4.8	0.27	3.4	0.40
13 32.09932	116.54785	18.3	7.1	0.85	0.94	0.94	4.3	116	37	140	2.3	204	155	235	7.1	0.11	4.7	0.09
<sup>a14</sup> 32.10913	116.53871	19.7	7.1	1.68	1.80	1.62	3.7	190	75	270	4.4	496	304	450	5.8	0.11	2.7	0.44
15 32.11187	116.53065	19.2	7.0	0.63			5.1	83	24	113	2.4	135	188	188	2.7	0.10	3.7	0.35
16 32.11598	116.53172	20.0	7.2	1.24	1.65		8.6	154	56	199	4.6	367	216	195	6.9	0.11	3.3	0.34
17 32.11758	116.52366	19.0	7.1	0.69			1.8	91	27	126	2.4	137	134	320	2.0	0.06	2.5	
18 32.12260	116.52473	20.4	7.0	1.30			4.9	172	59	193	3.5	414	226	283	6.4	0.04	3	0.55
19 32.12489	116.52742	21.3	6.9	2.32			4.9	265	120	279	4.7	921	359	330	7.0	0.06	18.6	0.63
<sup>a20</sup> 32.12580	116.53333	21.8	6.9	1.09	1.26	1.33	4.3	149	48	162	1.3	372	136	223	1.8	0.03	4.7	0.19
21 32.14429	116.51935	25.0	7.0	0.81			5.0	109	25	130	1.4	204	115	143		0.01	27.8	0.11
22 32.14018	116.51774	21.4	7.3	0.87			4.7	118	31	146	1.4	259	90	203	5.1	0.09	77.4	
<sup>a23</sup> 32.13333	116.52796	21.6	6.7	0.83	0.89	0.85	5.8	115	27	141	0.5	222	102	204	0.1	0.04	3.8	0.23
24 32.11187	116.54355	21.6	7.1	1.49			6.9	168	66	205	1.5	593	79	296	4.4	0.03	4	
<sup>a25</sup> 32.09018	116.57688	19.2	7.3	0.68	0.73	0.73	4.3	108	24	119	2.5	88	181	269		0.03	23.2	0.15
27 32.08881	116.59355	21.5	7.5	1.97	2.17	2.17	7.7	211	93	295	4.5	572	223	450	5.9	0.04	1.1	0.31
28 32.11859	116.59471	24.2	7.2	1.00			7.7	138	34	144	2.9	351	57	240		0.01	104.7	10.50
<sup>a29</sup> 32.11257	116.59914	21.9	7.5	0.79	0.80	0.81	7.3	90	24	134	0.8	251	36	190	1.3	0.04	1.5	1.38
30 32.10910	116.60198	22.2	7.0	0.70			6.8	81	22	134	0.5	225	39	190	3.1	0.04	2.8	0.42
<sup>a31</sup> 32.08607	116.60000	21.1	7.3	1.92	2.05	2.06	2.1	221	97	286	4.6	455	471	452	9.5	0.09	3.9	0.53
<sup>a32</sup> 32.07808	116.60000	19.3	7.6	1.04	1.04	1.50	7.1	125	47	192	2.1	214	241	397	3.6	0.07	2	0.57
33 32.08516	116.61398	24.0	7.1	2.72			6.1	256	139	340	4.3	908	487	350	24.5	0.05	3.3	0.43
<sup>a34</sup> 32.09110	116.62634	24.2	7.2	1.10	1.20	1.26	7.4	110	37	203	1.3	408	53	200	5.7	0.03	5.4	0.79
<sup>a36</sup> 32.07169	116.61237	19.6	7.7	1.28	1.46	1.02	8.6	160	62	206	3.5	274	265	276	26.0	0.09	1.5	0.29
<sup>a37</sup> 32.06507	116.64570	20.4	7.1	2.03	2.16	2.18	6.5	204	88	293	3.0	715	274	307	10.6	0.05	4.1	0.52
<sup>a38</sup> 32.04204	116.63139	21.3	7.5	0.41	0.65	0.64	7.6	38	12	87	1.1	119	18	143	3.8	0.18	5.6	0.44
39 32.04475	116.64355	20.2	7.2	0.88			6.1	81	34	161	1.3	344	53	112	8.0	0.16	2	0.57
<sup>a40</sup> 32.06448	116.59599	21.0	6.7	0.44	0.48	0.48	5.1	49	15	83	1.1	137	24	118	3.5	0.08	7.4	0.12

The results for TDS are also given for April and November 2002

<sup>a</sup>Sites analysed for trace metals during the November 2002 sampling and described in Table 2

**Fig. 2** Regional distribution of TDS concentrations ( $\text{g l}^{-1}$ ) in water from 37 wells from the Guadalupe aquifer in September 2001



Ca-Na-Cl composition, and (b) waters with low TDS concentrations ( $< 1 \text{ g l}^{-1}$ ), which have a Ca-Na- $\text{HCO}_3$ -Cl composition (Fig. 4). Bicarbonate-type water is found adjacent to the main natural recharge sources and becomes enriched in Cl in most of the wells in El Porvenir and Calafia grabens. The hydrogeochemical fingerprint and the quality of water in the Guadalupe aquifer is better explained by Stiff diagrams plotted for each site (Fig. 1). The dominant anion is Cl in all the samples, except at those sites located near the recharge sources along the Guadalupe riverbed near Cañón Agua Caliente, as well as near Cañón El Mogor. However, despite having low TDS concentrations, water from the Cañada el Trigo is relatively enriched in Cl and, unlike other Cl enriched samples from this aquifer, it is not enriched in  $\text{SO}_4$ . Sulphate is significantly enriched in several samples from the El Porvenir and some from the Calafia region. At these sites  $\text{HCO}_3$  is commonly depleted compared to Cl and  $\text{SO}_4$ . Calcium is slightly enriched compared to Na and Mg in samples from the northern Calafia Graben and the Cañada El Trigo sub-basin. The water from a local spring in Cañada El Trigo (which also has relatively high Cl concentrations) is associated with a NE-SW striking fault cutting into this sub-basin (sample 28). Unlike the Calafia Graben region and Cañada El Trigo, Ca enrichments are not common in the El Porvenir region, yet they are relatively enriched in Na (except for sites 36 and 31). Furthermore, compared with the water composition in 1977 and 1990 (Table 2), major ion concentrations have remained relatively unchanged, with the highest concentrations of all the major ions found in El Porvenir region, probably as a result of longer residence times. Tritium

concentration in water from El Porvenir (sample 36) is below the 1.9 TU detection limit used, and is therefore interpreted as being sub-modern, recharged prior to 1952, or representing a mixture between sub-modern and recent waters. Water from the Calafia Graben, however (sample 15), has a tritium activity of 3.6 TU and is interpreted as being of recent ( $< 5$ – $10$  years) recharge (Clark and Fritz 1997).

#### Phosphate and iron

The concentrations of  $\text{PO}_4$  (expressed as P- $\text{PO}_4$ ) range from 0.0 to  $0.3 \text{ mg l}^{-1}$ . Samples with high TDS concentrations ( $\text{TDS} > 0.88 \text{ g l}^{-1}$ ) always have low  $\text{PO}_4$  concentrations ( $\text{PO}_4 < 0.1 \text{ mg l}^{-1}$ ; Fig. 5). Consequently,  $\text{PO}_4$  concentrations that exceed background levels ( $> 0.1 \text{ mg l}^{-1}$ ) are only found in some samples with low TDS and low temperature, such as the groundwater collected near the Cañón Agua Caliente recharge area, and to a lesser extent, the groundwater collected northwest of Cañada el Mogor (samples 38, 39 and 40). It is likely that  $\text{PO}_4$ -enriched water is being supplied to these sites from the nearby recharge sites, as suggested from their low TDS and low temperatures. Unlike the slight enrichment near Cañada el Mogor in the western aquifer, maximum  $\text{PO}_4$  concentrations west of Cañón Agua Caliente (along the Guadalupe riverbed) are not found immediately adjacent to a recharge area, but  $\sim 2 \text{ km}$  to the west.

Dissolved phosphate in groundwater is commonly associated with discharge from sewage treatment plants,

**Table 2** Ranges in concentrations of major ions, nutrients, metals and metalloids in groundwater from the Guadalupe Valley in 2001, 1990 and 1977, and comparison with the Mexican and USA maximum permissible levels for drinking water

Year	TDS (g l <sup>-1</sup> )	Ca (mg l <sup>-1</sup> )	Mg (mg l <sup>-1</sup> )	Na (mg l <sup>-1</sup> )	Cl (mg l <sup>-1</sup> )	SO <sub>4</sub> (mg l <sup>-1</sup> )	CaCO <sub>3</sub> (mg l <sup>-1</sup> )	N-NO <sub>3</sub> (mg l <sup>-1</sup> )	P-PO <sub>4</sub> (mg l <sup>-1</sup> )	Fe (µg l <sup>-1</sup> )	As (µg l <sup>-1</sup> )	Cd <sup>a</sup> (µg l <sup>-1</sup> )	Cu <sup>a</sup> (µg l <sup>-1</sup> )	Pb <sup>a</sup> (µg l <sup>-1</sup> )	Mo <sup>a</sup> (µg l <sup>-1</sup> )	Zn <sup>a</sup> (µg l <sup>-1</sup> )	Se <sup>a</sup> (µg l <sup>-1</sup> )	Sb <sup>b</sup> (µg l <sup>-1</sup> )
2001	0.4–2.7	28–264	12–139	83–340	88–921	18–487	92–371	0–26	0–0.3	1.1–105	0–10.5	0–1.15	0.02–4.3	0.02–2.7	0.02–18	0.03–39	0.02–70	0–1.02
1990 <sup>b</sup>	0.4–4.6			51–959	78–1534	19–1402	73–610											
1977 <sup>c</sup>	0.4–3.0	4–68	1.7–113	8–622	17–972	19–567	7.3–49											
NOM <sup>d</sup>	1.0			200	250	400	500	10		300	50	5	2000	25	5000	5000	50	50
EPA <sup>e</sup>				250	250	250		10		300	10	5	1300	15	5000	5000	50	50

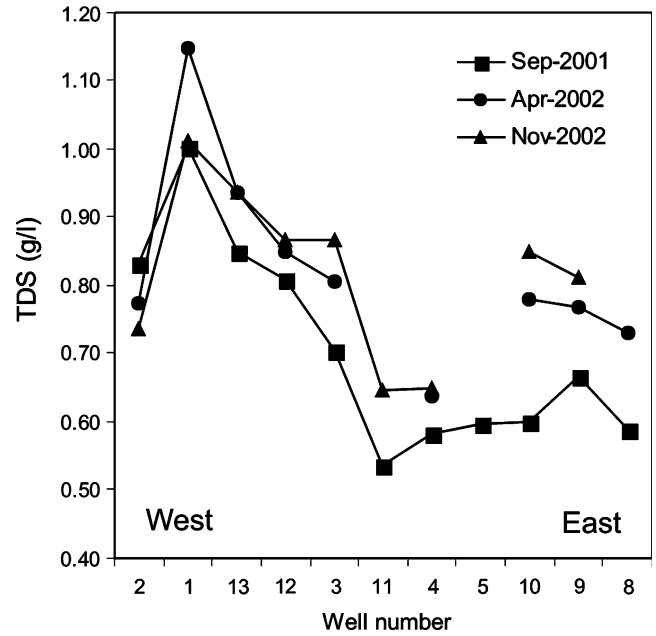
<sup>a</sup>Elements analysed only for the November 2002 survey

<sup>b</sup>CNA (1991)

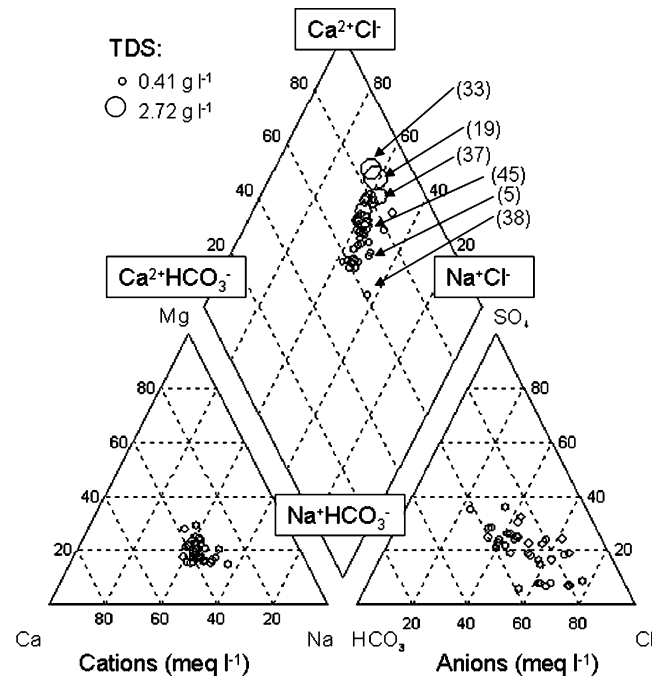
<sup>c</sup>SRH (1977)

<sup>d</sup>Mexican Official Norm (Diario Oficial de la Federación 1999)

<sup>e</sup>EPA (2003)



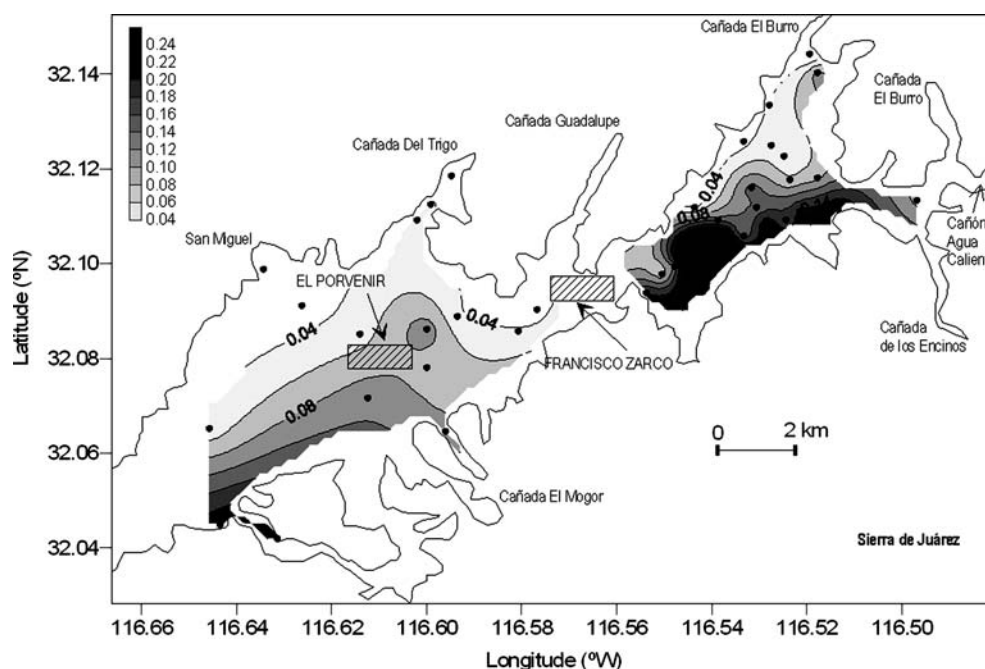
**Fig. 3** Temporal evolution of TDS concentrations in September 2001, April 2002 and November 2002, in water from 11 wells used for urban supply (CESPE) aligned W-E westward of the water recharge site near Cañon Agua Caliente and used for urban supply



**Fig. 4** Piper diagram for the major ion composition of water from 37 wells from the Guadalupe aquifer, indicating water type and its association with TDS concentrations

leaking septic tanks and manure pits (Le Blanc 1984; Zanini and others 1998; Krapac and others 2002). Urban centres in the valley (El Porvenir and Francisco

**Fig. 5** Regional distribution of P-PO<sub>4</sub> concentrations (mg l<sup>-1</sup>) in water from 37 wells from the Guadalupe aquifer in September 2001. The inset shows a bivariate plot between the concentration of TDS (g l<sup>-1</sup>) and P-PO<sub>4</sub> concentrations, suggesting an association between water with <1 g l<sup>-1</sup> TDS and higher P-PO<sub>4</sub> concentrations



Zarco; Fig. 5) do not have sewerage facilities or wastewater treatment plants and, therefore, rely entirely on septic tanks, a potential contamination source to the aquifer. The P-PO<sub>4</sub> concentrations in the aquifer do not exceed 0.3 mg l<sup>-1</sup>, being at least one order of magnitude lower than the concentrations in known contaminated sites (Le Blanc 1984). The lack of any correlation between P-PO<sub>4</sub> and N-NO<sub>3</sub> concentrations (or any other element in this study), suggests that the slight enrichments of P-PO<sub>4</sub> in the Guadalupe aquifer are caused by hydrogeologic rather than anthropogenic processes. These processes can be controlled by the adsorption/desorption of phosphorus in the aquifer sediments (Le Blanc 1984; Walter et al. 1996). Phosphorus adsorbed on aquifer sediments may be desorbed as a result of water with low pH and low conductance (clean water) flushing through a previously contaminated aquifer (Walter et al. 1996; Stollenwerk and Parkhurst 1999). However, in the present study, waters with PO<sub>4</sub> concentrations above the background 0.1 mg l<sup>-1</sup>, have pH values that range from 7.01 to 7.46, similar to the average pH in the aquifer, which is 7.28. Thus, the increase in dissolved PO<sub>4</sub> cannot be associated with low pH. Furthermore, high dissolved reactive phosphorus concentrations in groundwater adjacent to a riparian zone have been associated with low Fe<sup>2+</sup> and low dissolved oxygen (DO) concentrations (Carlyle and Hill 2001). In the Guadalupe aquifer, dissolved P-PO<sub>4</sub> does not show any correlation with total dissolved Fe, but it does show a negative (but non-significant) correlation with DO, suggesting that the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> (probably bacterially induced) could be responsible for the slight increases in dissolved PO<sub>4</sub> shown in Fig. 5 (Moore and Reddy 1994).

Arsenic, selenium and trace metals

Results for the regional distribution of As in the Guadalupe aquifer (Tables 1, 2) suggest that higher concentrations of this element are found in wells located in the northern limit of the basin. Although as concentrations are low (average = 0.5 µg l<sup>-1</sup>) and are often below the detection limit, localised inputs to the aquifer are evident. One such source is located in the narrow Cañada El Trigo sub-basin where the only sample (28) collected from a spring (not thermal) has a concentration of 10.5 µg l<sup>-1</sup> (near the permissible limits of the US-EPA drinking water guidelines but still below the Mexican official norm; Table 2). This spring is associated with a NE-SW striking fault, which cuts into the sub-basin, through which water may be supplied. The two additional wells sampled in this sub-basin (south of the spring) have much lower As concentrations but are still above background levels (1.38 and 0.42 µg l<sup>-1</sup>), probably due to dilution by local runoff during rainy periods. Although water temperature in this sub-basin does not suggest a direct geothermal source (Smedley and Kinniburgh 2002), its association with a fault supports the possibility of As leaching during high temperature reactions at greater depths within the fault system. Geothermal water has commonly been associated with high As concentrations in the western USA (Welch and others 1999). Striking faults NE-SW are common in the granodiorite terrain to the North of the Guadalupe basin and are responsible for shaping at least three of the major canyons there (El Trigo, Guadalupe and El Burro). These faults also cut through volcanic and meta-sedimentary rocks approximately 7 km north of the

Guadalupe basin. Water from Cañada El Trigo has a slightly different hydrogeochemical fingerprint than water from the rest of the aquifer as well as lower TDS concentrations. Arsenic results tend to confirm the peculiarity of this water.

Of the trace metals and metalloids studied, only Se (70 µg/g) in sample 36 exceeds the EPA 50 µg/g maximum contaminant level for drinking water. This sample is located in El Porvenir and has the highest concentrations of Cu (4.4 µg/g) and Mo (18.1 µg/g), as well as N-NO<sub>3</sub> (Tables 1 and 2). These elements are commonly used in agricultural fertilizers and are, except for Cu, highly mobile in groundwater under both oxidizing and reducing conditions (Reimann and Caritat 1998). Although tritium results indicate a sub-modern age for this sample, the high concentration of these elements, suggests infiltration and mixing of water derived directly from the irrigation of crops located above this well. Contamination of this part of the aquifer by the use of fertilizers is likely. Overall, no other significant metal enrichments are found in the aquifer.

## Summary and conclusions

Groundwater in the Guadalupe aquifer is classified in two main compositional types: (a) water with TDS > 1 g l<sup>-1</sup> commonly with a Ca-Na-Cl composition and (b) water with TDS < 1 g l<sup>-1</sup> and a Ca-Na-HCO<sub>3</sub>-Cl composition. Based on its composition, it can be suggested that water is not only being recharged during rain periods through the Guadalupe riverbed (to the west of Cañon Agua Caliente), but also south (near Cañada el Mogor) and north of the basin (Cañada el Trigo). Other additional recharge sites are likely. Unlike nitrate, phosphate is associated with fresh (TDS < 1 g l<sup>-1</sup>), relatively colder water near the recharge sites adjacent to Cañon Agua

Caliente and Cañada El Mogor, suggesting peculiar hydrogeochemical processes in these areas. A relative depletion in HCO<sub>3</sub> and a concomitant enrichment in Cl in those waters with higher TDS concentration are thought to result from longer water residence times, especially in El Porvenir graben, where the highest TDS, major ions, as well as fertilizer derived N-NO<sub>3</sub>, Se, Mo and Cu concentrations are found. Tritium analyses suggest that water is of pre-modern age in the El Porvenir graben and of recent age in the Calafia graben closer to the main recharge site. Mixing with local contaminated water used for irrigation is likely in El Porvenir. Small water quality variations (generally < 10%) were detected throughout the period studied (2001–2002), suggesting that reduced rainfall and recharge did not have a significant effect on water quality. However, those wells used for urban supply which are located near the Cañon Agua Caliente recharge area show a slight but constant increase in TDS, probably from the uninterrupted extraction of water from the aquifer adjacent to its main recharge area. Wells with As concentrations above background are identified near the northern limit of the basin with as values as high as 10.5 µg l<sup>-1</sup>. This cold spring is associated with a NE-SW striking fault, which cuts, into the sub-basin, suggesting a geothermal source for this element.

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