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Rapid isotopic changes in groundwater, upper Rio Guanajuato catchment, Mexico

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RESUMEN

Cambios isotópicos significativos en el agua subterránea de la cuenca alta del Río Guanajuato, México, fueron detectados en dos conjuntos independientes de muestras que incluyeron al 3% de los 1600 pozos de alta producción del área. Los muestreos se realizaron en diciembre de 1998 (53 muestras) y en julio - agosto del 2003 (41 muestras). La concentración promedio dell deuterio no cambió entre 1998 y 2003, pero la del oxígeno-18 sugiere una dilución generalizada del agua profunda por infiltración de la precipitación local. Este cambio regional ocurrió dentro de 56 meses, indicando un sistema hidrogeológico muy dinámico. La rápida recuperación del almacenamiento acuífero o el bombeo insostenible de reservas acuíferas viejas son explicaciones posibles.

PALABRAS CLAVE: Cambio isotópico reciente en el oxígeno-18 y el deuterio del agua subterránea, evolución acuífera rápida, Guanajuato, México.

ABSTRACT

Significant changes in the isotopic composition of groundwater in the upper catchment of Rio Guanajuato, Mexico, were detected in two independent sets of samples for 3 % of the 1600 high–production wells in the area. Sampling was done in December 1998 (53 samples), and in July – August 2003 (41 samples). Average deuterium concentration did not change between 1998 and 2003 but the average oxygen–18 concentration suggested a generalized dilution from deep water from infiltrated local precipitation. This regional change occurred within 56 months, indicating a highly dynamic hydrogeologic system. Fast replenishment of aquifer storage, or non sustainable over–pumping of old aquifer reserves, are possible explanations.

KEY WORDS: Recent isotopic change in oxygen–18 and deuterium in groundwater, rapid aquifer evolution, Guanajuato, Mexico.

1. INTRODUCTION

Intense extraction of groundwater resources may result in a noticeable drawdown of the water level and significant changes in the hydrodynamics of aquifer systems, including flow directions and velocities, and recharge and discharge patterns. Perceptible effects include decreasing well yield, changes in vegetation, or the disappearance of springs and creeks. Changes may also be detectable in the groundwater composition itself. The natural isotopes oxygen-18 and deuterium have been proven useful in the past to detect different recharge and flow components (Sidle, 1998; James *et al.,* 2000; Bryson *et al.,* 2004). Here they are used as indicators for changing groundwater dynamics due to heavy extraction.

The present study compares two sets of oxygen-18 and deuterium concentration data ($\delta^{18}O$ and $\delta^{2}H$, in per mil versus Vienna–SMOW, see Gonfiantini, 1977), belonging to groundwater extracted from the upper catchment of the Guanajuato river in central Mexico (Figure 1), an area of intense groundwater extraction.

The objective is to document changes in the isotopic composition of extracted groundwater occurring between December 1998 and July to August 2003. Since the geographic extension of the catchment area is measured in hundred of square kilometers, the hydrological process to be described might be remarkable by its celerity, and the implications could be important.

Source data are found in two technical reports: CEASG (1999), a study ordered by the Water Commission of the Government of the State of Guanajuato; and COREMI (2004), a study performed by the former Council of Mineral Resources of the Federal Government of Mexico in collaboration with the National Autonomous University of Mexico (UNAM), with direct participation of the present authors. A preliminary version of this study is found in COREMI (2004) and included in Kralisch (2004).

2. STUDY AREA

The upper Rio Guanajuato catchment is located in the state of Guanajuato, central Mexico. The main economic activities are agriculture (with about 80% of total water use), and to a lesser extent industry, mining and tourism. Increasing water demand originates from fast growing cities such as Leon (Figure1).

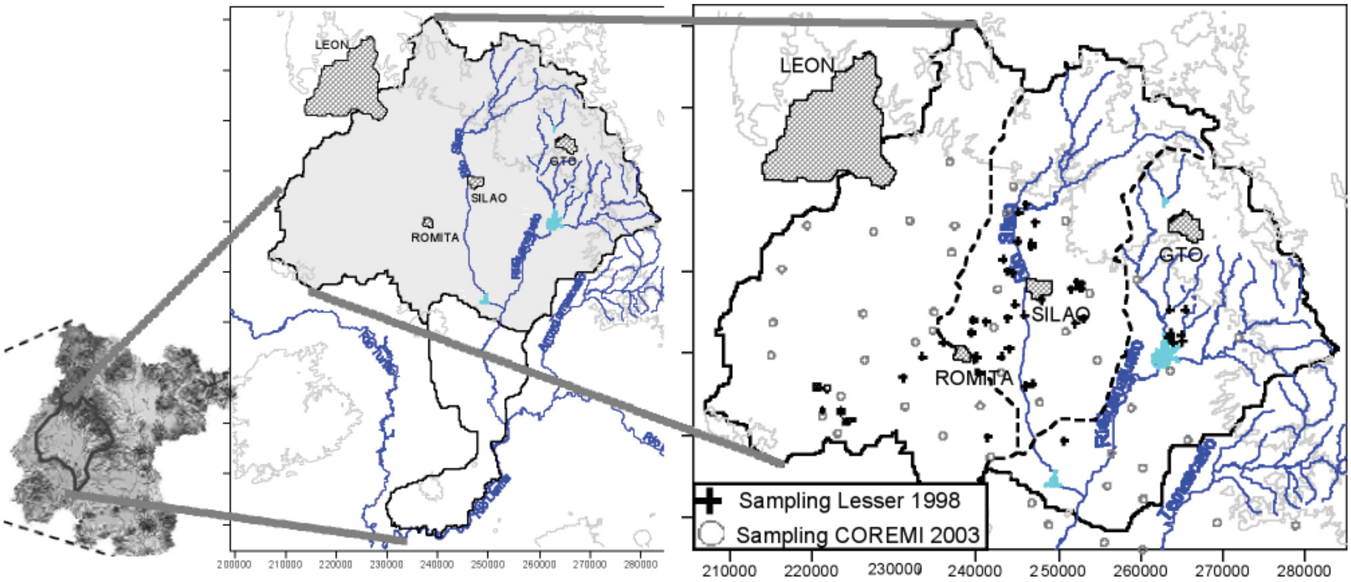

Fig. 1. The Rio Guanajuato catchment in the State of Guanajuato, Mexico. Distribution of the deep pumping wells where water samples have been taken in December 1998 by Lesser for CEASG (1999) and in July-August 2003 by the Mining Resource Council (COREMI, 2004).

Elevation ranges between 1760 *m asl* (meters above sea level) and 2950 m asl. The study area is characterized in the north by a dense surface–drainage network in the Sierra de Guanajuato. Surface water flows towards the lowlands in the south of the catchment and drains into the Rio Guanajuato, Rio Silao and San Juan de Otates creek, feeding Rio Lerma. Most of the creeks in the area are intermittent or ephemeral whereas Rio Guanajuato and Rio Silao are perennial streams with highly varying discharge.

The climate is semiarid with rains in the summer. In the dry season, from November to April, the rainfall usually is less than 10 % of the amount accumulated during the whole year (García, 1988). In the lowlands, long–term annual average values of precipitation and temperature are ~ 600 mm and ~ 19 °C, respectively. However, since 2000, central Mexico and northern Mexico have experienced some extraordinary rainy years (Méndez, 2005). This meteorological phenomenon is waiting to be studied.

The hydrogeological basin is mainly formed by a graben of 400 – 800 m depth ("Graben de Leon"). It is bounded by a horst, the Sierra de Guanajuato, and an extensive normal fault system ("Falla Bajio") in the NW, as well as by consolidated blocks and faults in the W and SW. Hydrogeological connection exists with the adjacent hydrographic Rio Turbio basin and towards the SE (COREMI, 2004).

The graben is filled with alluvial and lacustrine deposits of diverse grain size and a thickness of 200 – 400 m, followed by ~ 400 m of fractured rhyolitic rocks, tuff and ignimbrites. Outcrops of the latter unit in mountain- and hill ranges presumably act as important recharge zones within the system.

Most of the wells are located in the granular medium. However, the rhyolites and ignimbrites do have a high storage capacity. Pumping tests suggest Darcy velocities of 14.6 – 204 m/y in the granular material, and 3.65 – 1160 m/y for the fractured medium (COREMI, 2004). These high differences show the importance of faults and fractures for the region's groundwater flow, which agrees with the geologic information in the region (CEASG, 1998; Ibarra, 2004). Besides, bulk horizontal groundwater flow tendency originally followed the river pathways from the NE to SW, but this trend has been locally inverted by deep cones of extraction, with Silao and Irapuato as the most affected areas.

Groundwater is the region's basic resource. There are about 1600 wells evenly distributed in the agricultural valleys and plains of Silao–Romita. In the municipality of Silao alone, 587 wells deeper than 100 m were counted, with a total extraction of more than 220 Mm^3 / year (CEASG, 1998). Because of irrigation most of the groundwater is extracted in the dry season. As in many aquifers of northern and central Mexico, water production at the present rate is not sustainable (Alley *et al.*, 1999). Groundwater levels have declined up to three meters per year. However, since 2002 this decline has diminished and was even reversed in some areas (COREMI, 2004).

Water temperature in wells is between the environmental media and 44 °C, to be shown later on. There are no known indications of well water temperature changes during the last decades. Regional geothermalism has its most important natural manifestation in the eastern piedmont of Sierra de Guanajuato, at the Comanjilla hot spring and spa. The high temperatures are most probably associated with the geological structures described above.

3. SAMPLING AND LABORATORY ANALYSIS

Sampling. Data correspond to two periods of well water sampling in the catchment. Altogether, roughly, 3% of the producing wells were sampled. The first set of observations included 53 wells and was performed in December 1998 during the dry season (CEASG, 1999). The second set included 41 wells sampled in July and August 2003, in the early rainy season (COREMI, 2004).

Sampling in both periods was independent but similar. Both were intended to monitor the isotopic composition of the groundwater. The samples in both collections were not from the same wells (Figure 1). In the interval of 56 months between both periods of sampling, there was no information on significant changes in the condition and amount of groundwater extraction.

Sampling procedures of the first sampling are explained in CEASG (1999). One of us (AC) participated in the second sampling. In both cases, wells were in the middle of routine operation, most of them pumping continuously for days, weeks, and even longer: thus samples correspond to nearly steady–state pumping with stabilized water quality (Huizar *et al.,* 2004; p. 442). Each sample was collected at the well discharge; water temperature of some wells was measured in situ. Clean sealed plastic bottles were used. Shipment of samples to the laboratory was immediate; isotope analysis was done two or three weeks later.

Analysis. CEASG analyzed the samples at the University of Waterloo, Canada. COREMI made use of a laboratory at UNAM, in Mexico City. Both laboratories report results in deltas calibrated according to international standard (Gonfiantini, 1977; and Coplen, 1988). Results are presented in Appendix 1.

An international comparison of Waterloo and UNAM results was published by IAEA (1999). This report describes the laboratory methods and cross–checking analyses. Both laboratories have comparable results. There are no systematic errors between them, and the values presented in Table 1 are comparable. The analytical uncertainties at Waterloo and UNAM are ~ ± 0.1 ‰ for $\delta^{18}O$, and ~ ± 1.6 ‰ for $\delta^{2}H$.

4. OVERALL INDICATORS

Using the data from Table 1, four histograms with their respective Gaussian distributions were elaborated: two for deuterium (1998 and 2003), and two for oxygen–18 (1998 and 2003). See Figure 2A and 2B.

Let $<\delta(t)>$ symbolize the arithmetic average of all δ values on a sampling date t, and $\sigma(t)$ the corresponding standard deviation. A summary of these overall indicators appears in Table 1.

Table 1

Statistical comparison of two data sets (from December 1998 and July-August 2003) on the isotopic quality of the groundwater in the Upper Rio Guanajuato Catchment. The shift in oxygen–-18 mean concentration is clearly visible, standard deviations are similar in both years´ data pairs.

Sampling	**Oxygen-18**[§]			**Deuterium**[§]		
	n	$<\delta^{18}O>$	σ	n	$<\delta^{2}H>$	σ
December 1998[¶]	53	-9.82	0.44	53	-75.0	3.1
July-August 2003[**]	41	- 10.52	0.5	41	-75.0	3.5

§: Isotopic concentrations expressed in δ's (‰ *versus* Vienna-SMOW). n: amount of data pairs; <δ> arithmetic average; σ: Standard deviation. ¶: Source CEASG (1998). **: Source COREMI (2004).

From Figure 2 the following three relationships are observed.

- For oxygen–18 as well as for deuterium, the shapes of histograms are similar and the Gaussians are alike (Figures 2A and 2B). Moreover, $\sigma(2003) \sim \sigma(1998)$;
- $<\delta^{2}H(2003)> - <\delta^{2}H(1998)> = 0.0$ ‰.; ·and
- $<\delta^{18}O(2003)> - <\delta^{18}O(1998)> = - 0.70$ ‰.

These relationships summarize what is to be called an overall shift of oxygen–18, as seen in Figure 3.

The overall data sets of 2003 and 1998 were grouped into local clusters, so that geographically close data could be compared. All wells have a similar design; neighboring wells should tap the same aquifer unit. The oxygen–-18 shift was observed within local clusters as well, which suggest a temporal —rather than a spatial— character of the observed change.

5. - DISCUSSION

Our groundwater isotope data sets are taken from the same study area, with the same purpose, similar number

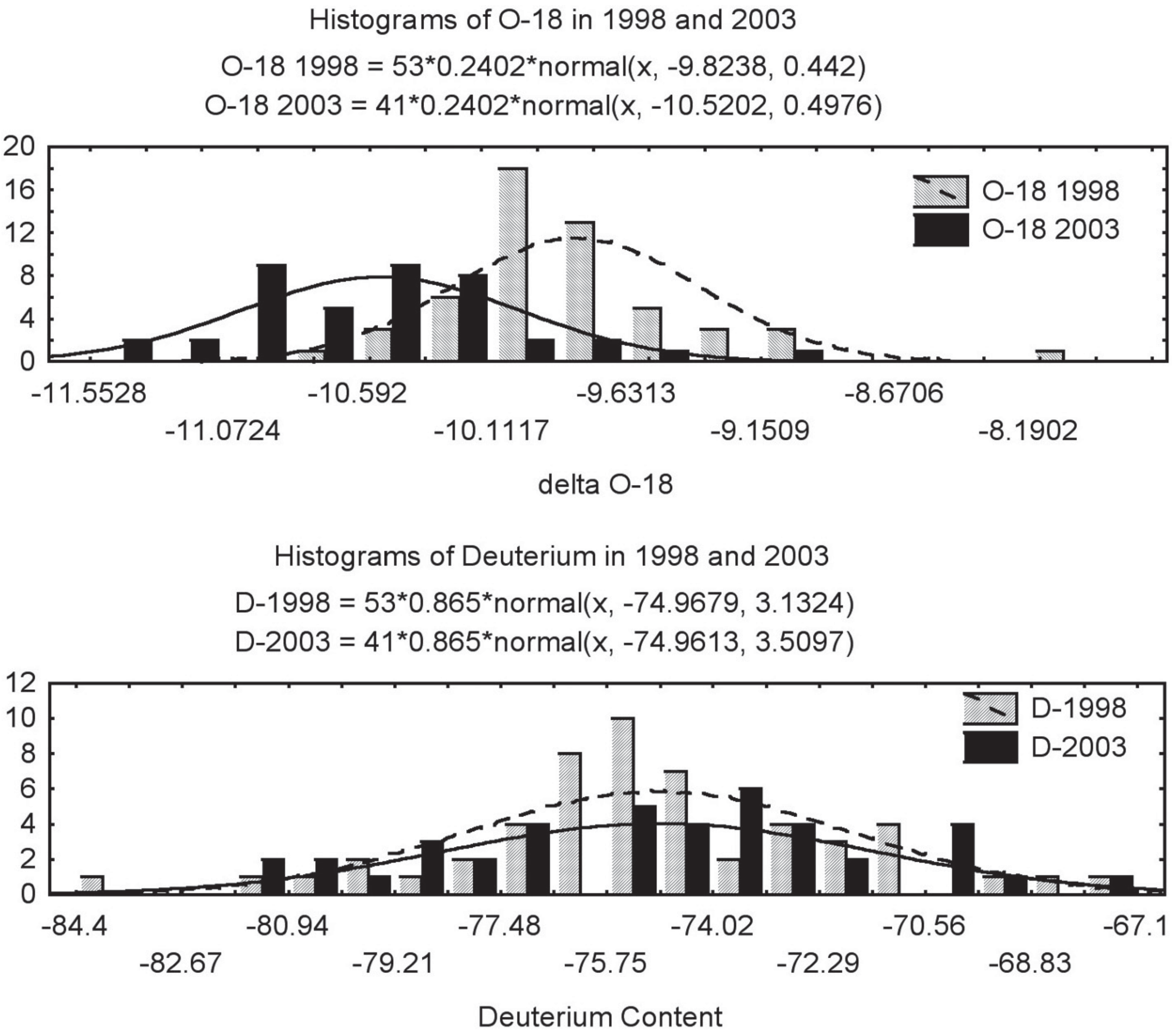

Fig. 2. Histograms and corresponding normal distributions of $\delta^{18}O$ (top) and $\delta^{2}H$ (bottom) values in deep well waters sampled in 1998 and 2003.

of samples, wells in steady–state operation, and identical sampling procedures, but with a difference in time of 56 months. There is no indication of systematic errors attributable to different laboratories. The shape of the resulting statistical distributions is similar, but there are analytically significant differences between some indicators.

Conclusion: Between December 1998 and July 2003, the isotopic concentration of the regional aquifer tapped in the upper Rio Guanajuato catchment changed significantly with an overall shift in oxygen–18. Graphically, in Figure 3, this shift brought the previous bulk of isotopic concentrations closer to the contemporary local meteoric values, $\delta^{2}H^{*} = 8\ \delta^{18}O^{*} + 11$ (Cortés *et al.,* 1997).

The isotopic change in groundwater for the entire catchment is thus a sound hydrogeological fact. To recognize its importance, interpretations of the process and its cause will be presented.

Process. The observed oxygen–18 shift brought the isotopic character of the extracted groundwater closer towards the signature of contemporary local precipitation (Figure 3). One indication for the cause of this peculiar process may be obtained from data of Comanjilla thermal spring. The isotopic composition of its water has changed in a way similar to the overall shift in the wells (Figure 3); and simultaneously, a partial cooling occurred (Table 2). The two phenomena together indicate a mixing process between waters of different

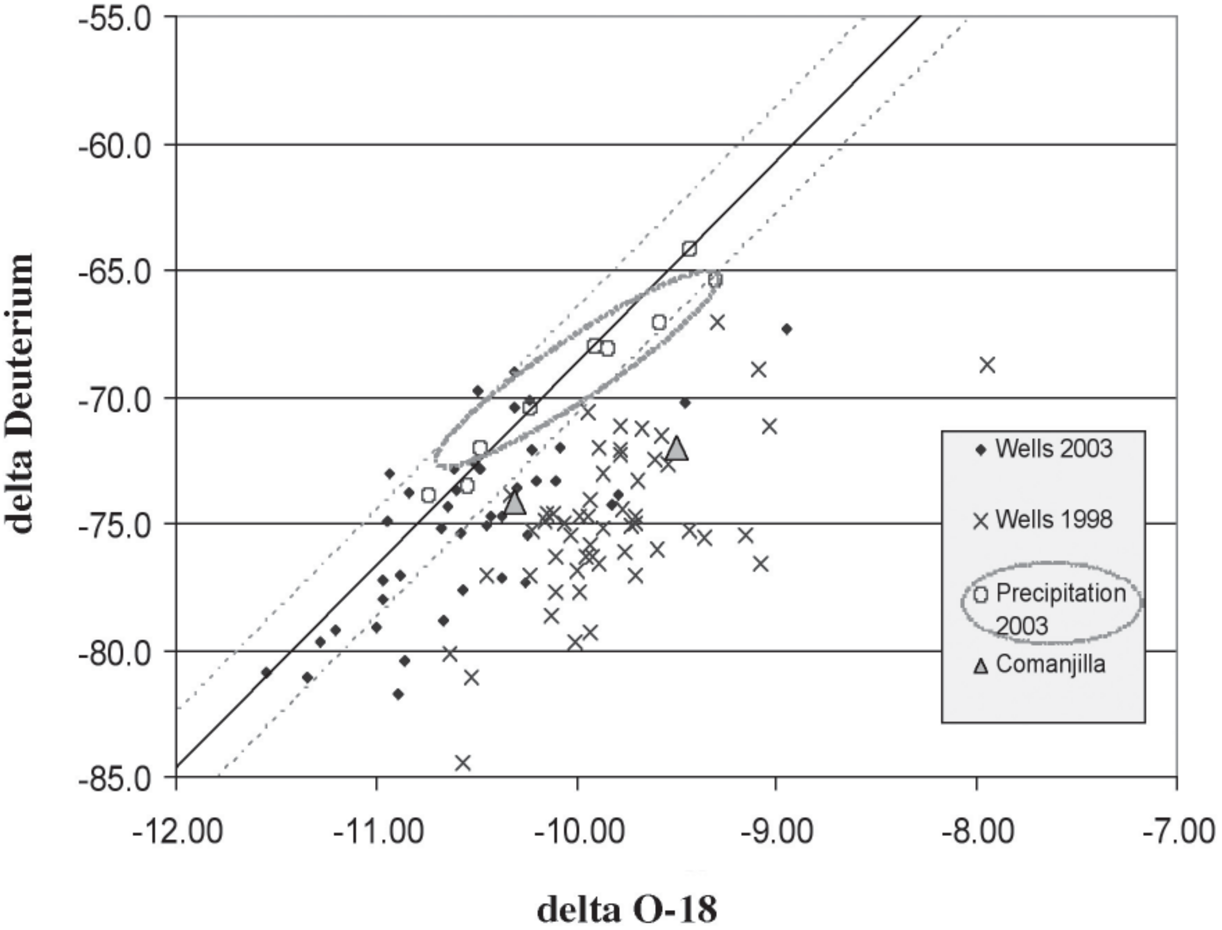

Fig. 3. $\delta^{18}O$ vs. $\delta^{2}H$ graph in relation to the local meteoric water line. An overall $\delta^{18}O$-shift towards the characteristics of local precipitation is clearly visible comparing the 1998 and 2003 well samples but also between the 2 values obtained from the Comanjilla spring.

temperature and composition. The cooler mixing component is gaining in relative importance.

This mixing hypothesis is supported by collateral evidence. Geochemical signatures (lithium, boron) and mixing–dilution trends of groundwater extracted in 1999 in La Muralla, an internal well field that will be mentioned below, correspond, after Johannesson *et al*. (2001), to geothermal water diluted by local precipitation. Furthermore, the trends of chloride and lithium concentrations —both conservative parameters— are compatible with the mixing of regional and local flows expected in the basin groundwater flow system of the study area (See: Ramos *et al.,* 2006).

The observed overall shift of the oxygen–18, thus appears to be an inverse process of a so–called oxygen-18 thermal shift, the latter being characterized by $\Delta\delta^{18}O > 0$ and $\Delta\ \delta^{18}H = 0$ (Truesdell and Hubbs, 1980), being a thermodynamic process of water–rock interaction. The oxygen–18 geothermal shift is spontaneously induced when an increase in temperature changes the isotopic water–rock equilibrium. Unlike an irreversible water–rock interaction that would cause the direction of the geothermal shift to move away from the meteoric line, the observed change is the result of a regional and contemporary process of induced mixture, as in Comanjilla and La Muralla.

Table 2

Variations in the isotopic concentrations and the temperature in Comanjilla spring waters confirm the observations made in the deep well samples.

Sampling	**$\delta^{18}O$ (‰ versus Vienna–SMOW)**	**$\delta^{2}H$ (‰ versus Vienna–SMOW)**	**Water temperature (°C)**
December 1998	- 9.50	-72.00	90
August 2003	- 10.39	- 73.6	78

Water extracted by most of the wells in the study region has two components. Water isotopically almost unaltered, whose origin is in local precipitation, is mixed with old water, isotopically altered by geothermalism and related to deep regional groundwater flows. The overall oxygen–18 shift is a consequence of a change in the mixing fractions of groundwater. The mixing fraction of recently infiltrated surface water has increased, or, equivalently, the mixing fraction of aquifer residual water has decreased.

The hypothesis of an increase of cold end member fractions is confirmed by the evolution of $\delta^{18}O$ and $\delta^{2}H$ as well as by the discharge temperature of Comanjilla hot spring. It is also supported by a trend of decreasing chloride concentrations shown for La Muralla by Ramos *et al.* (2005).

POSSIBLE CAUSES FOR THE ISOTOPIC CHANGE

A) As sampling operations were completed during the dry and rainy period, the isotopic change could reflect intrinsic seasonal variations in groundwater composition that had not been noted up to now. Those variations could be reinforced by anthropic alterations. During the dry season (e.g. December, 1998) well production is intensified. Due to high extraction rates and a lack of recharge from precipitation, groundwater levels decline and pumping is primarily concentrated on the deep layers of the tapped aquifer unit. These layers are saturated with old geothermal water that is isotopically altered. In the rainy season (e.g. July to August, 2003) the aquifer gets replenished and the volume to be tapped is likely to contain more rainwater component just infiltrated. The isotopic change would show the annual variation of the different components in the mixture (Table 3).

Nevertheless, this would require an extremely rapid response of the catchment aquifer system to seasonal recharge conditions, a fact that would highlight the significance of faults and fractures in the local subsurface flow, yet seems to be unlikely. Instead, there are reasons to suggest that the isotopic–hydrologic change, that is, the overall shift of the oxygen–18 in the groundwater in the upper Rio Guanajuato catchment (Figure 3), could be related to external alterations of a different kind. Two opposite explanations will be presented.

B) As documented before, groundwater exploitation in the study region is unsustainable. Recharge fails to compensate for extraction effects since decades ago. The effect is primarily a decline in the deep and isotopically altered groundwater components, whereas the local precipitation component is replenished every year. Ramos *et al.* (2005) inferred a process of non–renewable groundwater mining from the declining chloride concentrations in La Muralla well field west of the study area.

C) Conversely, one could also infer that the observed isotopic change signifies a recovery of the exploited aquifer. Instead of a decline of deep groundwater volumes, an increase in the precipitation component would be the reason for change in the mixture. Infrastructure and total groundwater production have kept unchanged during the last years, but static levels in some of the region's wells show an unexpected and continuous recovery (e.g. of 5 to 10 m between May 2002 and July 2003; COREMI, 2004). Regional isotopic change would be the local groundwater system's response to a period of several extraordinarily rainy years affecting central and northern Mexico (Méndez, 2005).

Considering either of the previous explanations, the changes in the local aquifer are much more dynamic than suggested by previous studies of the area (Cortés *et al.*, 2002). This observation is valid whether the isotopic change occurred in months or in a few years. The dynamics of the regional groundwater system might have some severe implications for the region's economic development. High infiltration capacity and fast recharge rates as required by explanations A and C would mean a high vulnerability of the aquifer to contamination. On the other hand, assuming explanation B to being the dominant process, the decline of the regional non–renewable groundwater resources would be even faster than expected. Water scarcity, soil erosion and other associated processes, would severely limit economic activity in the region.

ACKNOWLEDGEMENTS

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Appendix 1

Isotopic concentrations in δ's (‰ versus Vienna-SMOW) of oxigen-18 and deuterium found in water simples from deep wells in the Upper Rio Guanajuato catchment. Results stem from 2 different sampling periods in December 1998 and summer 2003.

CEASG (1998)	Oxygen-18	Deuterium
42	-10.0	-75
45	-10.1	-75
68	-9.7	-73
92	-9.1	-69
93	-9.6	-73
98	-9.9	-73
158	-10.0	-80
163	-9.4	-76
230	-9.7	-77
405	-10.5	-81
446	-9.7	-75
489	-9.2	-76
517	-10.2	-77
535	-10.6	-84
545	-10.1	-79
575	-9.7	-75
637	-9.9	-76
664	-9.8	-76
748	-10.0	-77
753	-10.5	-77
793	-10.3	-74
828	-9.9	-72
941	-9.8	-71
974	-10.2	-75
975	-9.9	-71
1015	-10.1	-75
1026	-10.2	-75
1102	-9.6	-72
1103	-9.3	-67
1191	-9.8	-72
1322	-9.5	-73
1379	-9.1	-77
1380	-9.9	-77
1381	-9.7	-71
1383	-8.0	-69
1385	-9.0	-71
1394	-9.9	-75
1405	-9.8	-72
1878	-10.1	-76
1916	-10.2	-75
1927	-9.4	-75
1928	-10.0	-78
1930	-10.6	-80
1931	-10.0	-76
1997	-9.9	-74
1998	-9.6	-76
1999	-9.9	-79
2001	-10.0	-76
2038	-10.1	-78
2071	-9.9	-76
10-SAPAL	-9.8	-74
1-SAPAL	-9.7	-75

COREMI (2003)	Oxygen-18	Deuterium	Water Temp.
I-091	-10.2	-76	27.4
I-088	-10.9	-81	23.3
I-086	-10.7	-82	33.4
I-084	-10.7	-79	27.3
I-041	-10.6	-75	24.3
I-038	-11.6	-81	25.7
I-037	-10.4	-75	36.2
I-036	-10.4	-77	25.5
I-035	-11.0	-79	24.2
I-034	-11.3	-81	25.9
I-033	-11.3	-80	22.6
I-022	-10.4	-75	25.9
I-021	-10.6	-75	22.7
I-020	-10.3	-70	27.3
I-019	-10.2	-73	26.4
I-018	-10.5	-73	27.2
I-017	-10.3	-74	25.4
I-016	-10.1	-73	25.3
I-015	-9.8	-74	28.1
I-014	-9.5	-70	21.7
I-013	-10.5	-75	26.3
-090	-9.0	-67	23.6
I-089	11.2	-79	24.9
I-076	-10.9	-75	31.0
I-075	-11.0	-78	27.9
I-043	-10.9	-77	22.8
I-042	-10.5	-73	22.0
I-040	-10.6	-74	25.4
I-039	-10.1	-72	20.5
I-025	-10.8	-74	24.9
I-012	-10.6	-74	25.8
I-011	-11.0	-77	23.4
I-093	-10.3	-77	26.8
I-095	-10.6	-78	44.0
I-092	-9.8	-74	28.9
I-050	-10.3	-69	29.3
I-032	-10.2	-72	55.2
I-027	-10.9	-73	25.5
I-026	-10.6	-73	30.1
I-024	-10.5	-70	28.2
I-023	-10.2	-70	25.9

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