

Geochemical and isotopic investigations on groundwater residence time and flow in the Independence Basin, Mexico.

J. Mahlkecht^{a,*}, J. Gárfias-Solis^b, R. Aravena^c, R. Tesch^d

^a *Centro de Estudios del Agua, Instituto Tecnológico y de Estudios Superiores de Monterrey, Ave. Eugenio Garza Sada No. 2501, C.P. 64849, Monterrey, Nuevo León, Mexico*

^b *Centro Interamericano de Investigaciones de Recursos del Agua, Universidad Autónoma del Estado de México, Cerro de Coatepec S/N, C.P. 50130, Toluca, Edo. de México, Mexico*

^c *Department of Earth Sciences, University of Waterloo, N2L 3G1, Waterloo, Ontario, Canada*

^d *Austrian Research and Testing Centre Arsenal, Environment Division, Faradaygasse 3, A-1030 Vienna, Austria*

}

author's version of the paper:

Mahlknecht J., Garfias-Solis J., Aravena R., Tesch R. (2006) Geochemical and isotopic investigations on groundwater residence time and flow in the Independence Basin, Mexico. Journal of Hydrology, vol. 324, Issues 1-4, p. 283-300, Elsevier ISSN: 0022-1694 <http://dx.doi.org/10.1016/j.jhydrol.2005.09.021>

* Corresponding author. *E-mail address:* jurgen@itesm.mx

Abstract

The Independence Basin in the semi-arid Guanajuato state of central Mexico is facing serious groundwater resources deficiency due to an increasing demand linked to a rapid population growth and agricultural development. This problem is aggravated by an inadequate evaluation of groundwater resources in the region. Geochemistry and isotopic tracers were used in order to investigate the groundwater flow system and estimate the groundwater residence time. The groundwater is characterized by low salinity with some exceptions associated to a contribution of more saline groundwater from deep formations. The predominant reactions are CO₂ gas dissolution, carbonate dissolution, albite weathering, kaolinite and chalcedony precipitation. Six principal hydrochemical zones were recognized, which provided information on plausible recharge sources and groundwater chemical evolution. The ¹⁴C concentration varies between 19 and 94 pmc. The high ¹⁴C values indicating recent recharge are observed at the basin margins and a trend to lower ¹⁴C values is observed along the modern groundwater flow paths. The groundwater residence time according to radiocarbon estimations ranges between recent and ~11 ka. The residence time distribution matches the regional important discharge zones west in the basin center (from Dolores Hidalgo and southwest from Doctor Mora). Hydrochemical tracers are in general agreement with the predeveloped and current hydraulic-head configuration however show some inconsistencies with the predeveloped head in the downgradient areas, which means that the impact by gradually increasing groundwater extraction during the last decades is reflected on radiocarbon age distribution. Geochemical evidences imply that the recharge input from the northern basin area is insignificant.

Keywords: Groundwater, Radiocarbon, PHREEQC, Semi-arid regions, Mexico

1. Introduction

The Independence Valley of semi-arid central Mexico, which relies greatly on groundwater resources, has experienced a massive population growth and agriculture expansion during

the last decades (SAGAR, 1999). State and local agencies have shown that the pressures imposed by growing population and socioeconomic development have resulted in declines in groundwater levels in excess of 0.8 to 1.2 m per year during the last decade (CEASG, 1999; CEAG, 2001). The production of 2,500 deep wells in the Independence Valley caused changes in groundwater flow direction, a continuous reduction of the number and discharge of springs and surface waters, and a deterioration of the ecosystem conditions (Navarro de León et al., 2005). Although this aquifer system is intensively exploited, little was known prior to this study about the flow pattern and groundwater ages. Similarly, the origin of elevated concentrations of some minor and trace elements and the vulnerability of the productive aquifer to pollution was unclear. This paper presents isotopic and chemical data from recent studies to corroborate the groundwater flow concept by evaluating radiocarbon data. These data concentrate on the upper sedimentary aquifer, because it is considered as the major potable water supply of the Independence Basin. The conceptual model obtained from the geochemical approach can be used to refine and calibrate the existing groundwater flow model, by means of comparing the hydrochemical patterns with the pathlines calculated via particle-tracking model, and the tracer residence times with the time of travel of particles along the pathlines.

2. Study Area

General Settings

The Independence Basin, situated in the Central Mexican Altiplano, is a sedimentary basin and covers a surface area of about 6,840 km², with the valley-floor-elevation of 1,850-1,900 and summits of 2,850 m above sea level (masl). The basin is surrounded by mountain ranges, which include the Sierra del Cubo to the north, the Sierra de Santa Barbara to the northwest, the Sierra de Guanajuato to the west, the Palo Huerfano and La Joya volcanoes to the south, the Zamorano massif to the southeast, and the Sierra de Xichú to the northwest (Fig. 1).

Mm³/year (CNA, 1992). Surface inflow from adjacent basins can be excluded. Numerous arroyos and ephemeral channels carry substantial water to the Rio Laja. These surface waters and mountain-front recharge are also responsible for recharge formation during heavy or long storm events. Rapid and direct infiltration to the basin deposits is insignificant.

For background of the geological settings of the Independence Valley and surrounding areas, the reader is referred to Martínez-Reyes (1992), Nieto-Samaniego et al. (1996), Pérez-Venzor et al. (1996), Vasallo et al. (1996), Aranda-Gómez and McDowell (1997), Cerca-Martínez et al. (2000), Eguiluz de Antuñaando et al. (2000), and Alanis-Ruiz (2002).

Aquifer Settings

The first diagnostic geohydrologic studies in the Independence Valley were carried out in the 1970's and 1980's (SARH, 1972; SARH, 1986). In light of the progressive groundwater level decline, Federal and State agencies conducted a series of studies beginning in the early 1990's to improve the hydrologic and geohydrologic understanding in the region (SARH, 1992; CEASG, 1999; CEAG, 2001; CEASG, 2000a, 2000b; UGTO, 2004). Some recent investigation results on the geohydrologic framework and hydrogeochemical conditions were published in PhD theses and research papers (Mahlknecht, 2003; Navarro de León, 2005; Mahlkecht et al. 2004a, 2004b; Navarro de León et al., 2005).

The aquifer system consists of the upper unconsolidated to moderately consolidated basin-fill deposits and the lower consolidated and fractured material (Fig. 2 and 3). The basin-fill deposits, with a thickness of up to 400–500 m, are composed of Pleistocene to Holocene alluvial deposits, and alluvial to lacustrine sandy to silty sediments, interstratified with volcanic conglomerates and tuffs from Pliocene. The tuff sequences represent an important formation because most water production wells are drilled in this geological unit. On the other hand, the lower fractured material consists mainly of ignimbrites of rhyolitic origin, along with conglomerates (*Guanajuato* conglomerate) and andesites (*El Cedro* andesite, *Allende* andesite) from Miocene-Oligocene age. The fractured aquifer material is important due to its high fracture density and potential infiltration capacity (UGTO, 2004). This study, however, is focused on the upper sedimentary deposits. Petrographic studies indicate that the siliciclastic aquifer consists mainly of quartz, albite, feldspar, kaolinite, Ca-

montmorillonite and hematite (Mahlknecht, 2003). Anorthite is found mainly in basaltic Quaternary formations in the south (San Miguel de Allende) and northeast (San Luis de la Paz) of the study area, whereas Ca-montmorillonite, chalcedony and kaolinite are mainly present in downgradient aquifer zones (toward the basin's center and the Allende dam). According to CEASG (1999), the tuff formations are of rhyolitic composition and consist mainly of quartz, K-feldspar, rock fragments and plagioclases. Calcite has been observed as the primary cement in sediments. A typical phenomenon of soils in some parts of the study area (e.g. Mineral de Pozos, Fig. 1) is the accumulation of calcium carbonate (*caliche*) immediately beneath the solum.

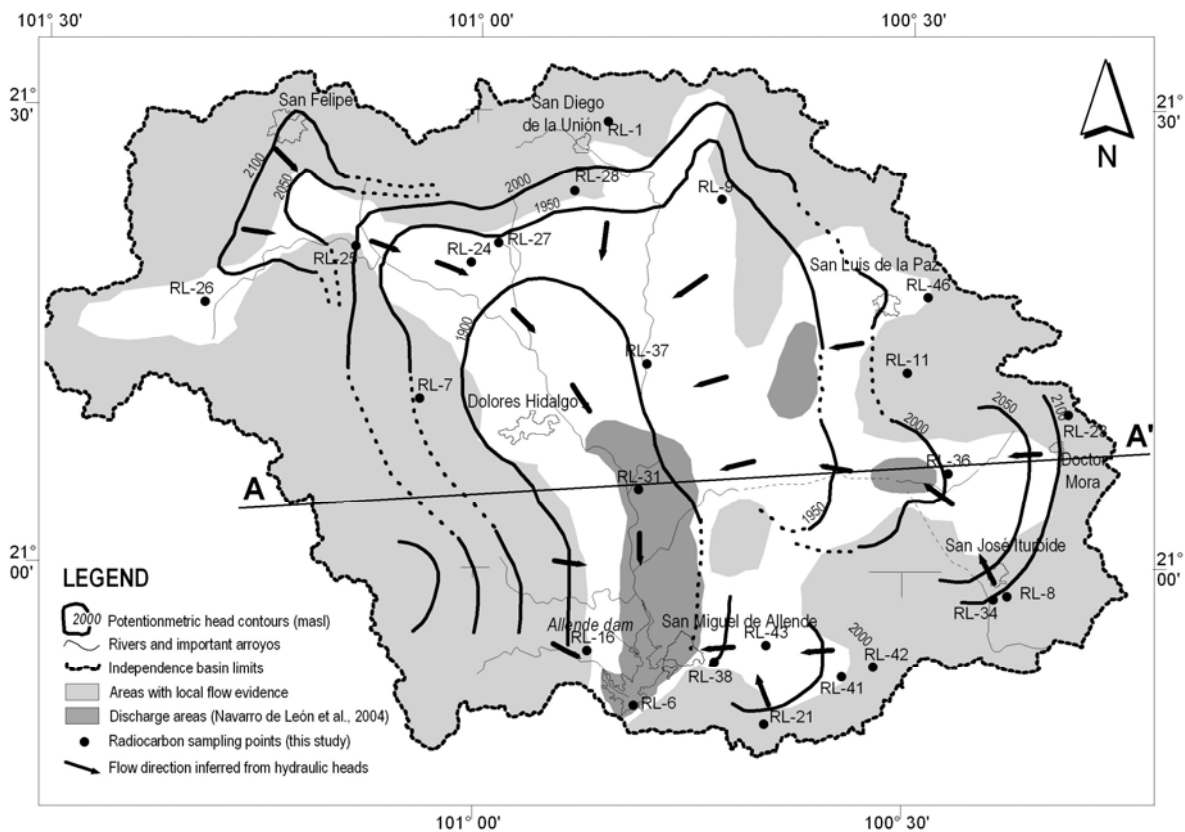


Figure 2: Groundwater flow concept under natural conditions and sampling sites.

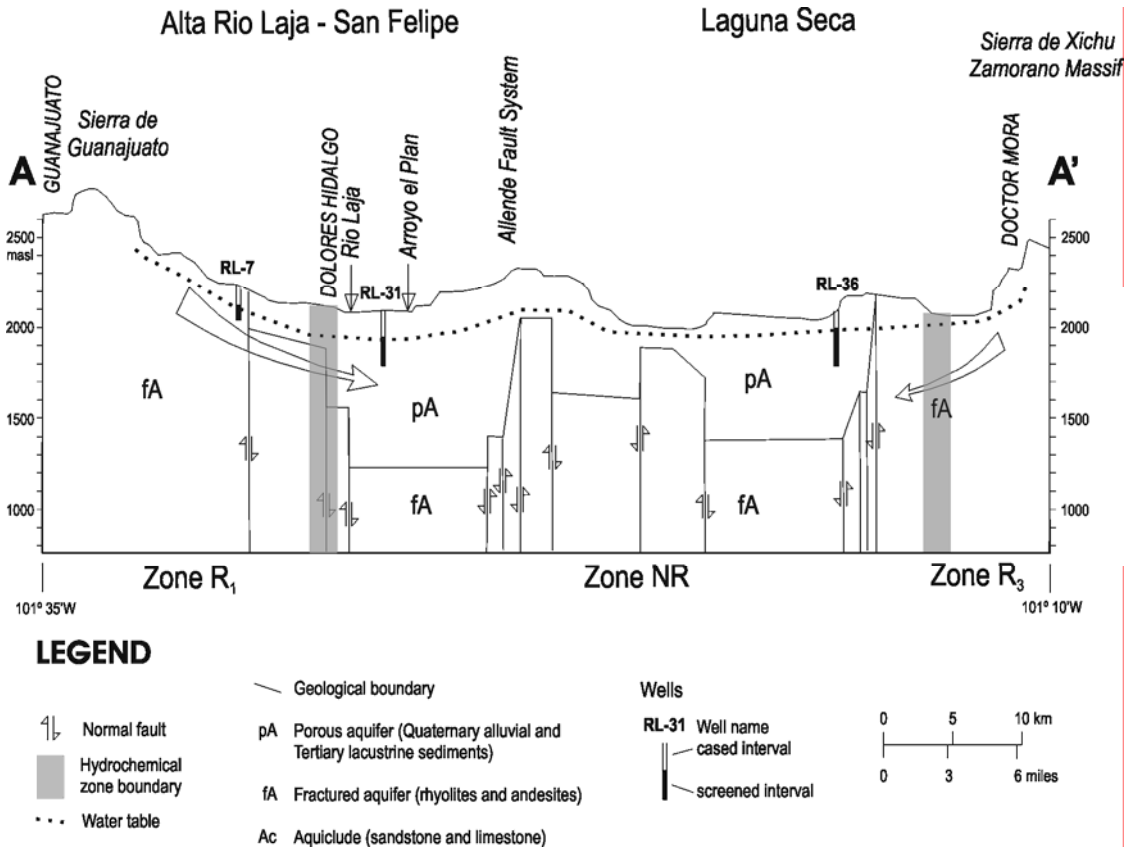


Figure 3: Simplified conceptual hydrostratigraphical section A-A' of the Independence aquifer (compare with Fig. 2) and hydrochemical zones (compare with Fig. 5).

3. Materials and Methods

Sample Collection and Analysis

Twenty-four samples were collected from agricultural and domestic water production wells from April 2000 to June 2000. Sampling and analyses procedures for major and minor chemical components are identical to those used in Mahlkecht et al. (2004b). An additional set of 40 chemical and 38 $\delta^{18}\text{O}$ data (Mahlknecht, 2003), as well as 35 chemical and 11 $\delta^{18}\text{O}$ data (UGTO, 2004), were used as background information.

The samples were analyzed for tritium by a liquid scintillation counter after electrolytic enrichment at Hydroisotop GmbH Laboratory, Schweitenkirchen, Germany. The detection limit was 0.6 Tritium Units (TU) and the analytical error varied around 0.6 TU. Oxygen-18

analyses were measured by ^{18}O by the Isotope Laboratory of the Institute of Geology at the Federal Technical Institute Zurich (ETHZ), Switzerland. Additional isotopic data analyzed by the Environmental Isotope Laboratory, University of Waterloo (UGTO, 2004) were included for spatial analysis. Analyses for ^{18}O are expressed in δ -notation relative to Vienna Standard Mean Ocean Water (VSMOW) standard. Radiocarbon analyses were carried out by liquid scintillation counting using the benzene technique. Carbon-14 data are reported as percent modern carbon with an analytical error in the order of 0.4 to 0.7 pmc. Carbon-13 was analyzed by mass spectrometry and the ^{13}C data are expressed in δ -notation relative to Vienna Pee Dee Belemnite (VPDB) standard. Both carbon isotope analyses were carried out at the Arsenal Research Isotope Laboratory, Vienna, Austria.

Eight carbonate samples (sample size 10 mg) were analyzed for ^{13}C and ^{18}O by mass spectrometry at the Environmental Isotope Laboratory of Waterloo University. The reported analytical error was 0.1‰. Carbon dioxide was prepared from carbonate minerals by reaction with 100% phosphoric acid (H_3PO_4) at 50°C.

Interpretation by Geochemical Modeling

Geochemical reaction models are used to account for the influence of carbon hydrochemistry in the ^{14}C dating, i.e. a piston flow model with the initial ^{14}C activity changed by the dissolution of “dead” carbonates in the soil zone. A speciation-solubility code, PHREEQC (Parkhurst and Appelo, 1999), version 2.11 (2005) was used to evaluate the equilibrium state of groundwater with respect to mineral and gaseous phases. In addition to the mineralogical investigation, chemical and petrographic data from other studies were compiled to reconstruct the chemical composition of rocks and soils (CEASG, 1999; Ramos-Ramírez et al., 2002; Mahlknecht, 2003; Ornelas-Soto, 2003; UGTO, 2004). UGTO (2004) reported also cation exchange capacity and exchangeable cations (Na, Ca, Mg, K). Morphological studies on scanning electron microscope (SEM) images were performed by Mahlknecht (2003) to evaluate dissolution or precipitation tendencies of the aquifer material. All these data were analyzed systematically and integrated to determine the geochemical reactants present in the Independence Aquifer.

For the geochemical modeling procedure, the sample set was initially divided into recharge samples and non-recharge samples. The criteria for this classification included the position

of the well with respect to the groundwater flow system, the saturation state with respect to carbonate mineral phases, and the carbon-14 activity. Recharge samples were determined to be substantially undersaturated with calcite ($SI < -0.7$) and dolomite ($SI < -2.0$), and/or to have high ^{14}C activities (>80 pmc). On the other hand, non-recharge samples include wells from intermediate and discharge zones, which are saturated with carbonates and have lower ^{14}C values (Table 1). Some samples are located at the limit between recharge and intermediate areas, but due to their chemical and isotopic characteristics are accounted for as discharge water samples. RL-9 and RL-24 represent intermediate water flow regimes and show mixed chemical and isotopic conditions between recharge and discharge water. RL-6, RL-31b and RL-36b are the only samples located directly inside or near the defined discharge areas (Fig. 2). The delimitation of recharge and non-recharge wells by means of ^3H and nitrate concentrations was not effective due to the low concentration and little variability.

Table 1: Chemical and isotopic data of samples used for evaluation of residence time. “RW”/“NRW” indicates the classification of samples into recharge and non-recharge samples.

SAMPLE ID	Well depth (m)	WT depth (m)	Position	Temp (°C)	pH	EC (µS/cm)	Cations (mmol L ⁻¹)								δ ¹⁸ O (‰ VSMOW)	³ H (T.U.)	log P _{CO2}	SI _{calcite}	SI _{dolom.}	
							Na	K	Mg	Ca	SiO ₂	HCO ₃	Cl	NO ₃						SO ₄
RL-1	14	12.0	NRW	16.6	7.86	542	1.92	0.36	0.49	1.04	1.03	4.75	0.43	0.04	0.09	-10.58	<0.6	-2.5	0.4	0.4
RL-6	60	36.1	NRW	26.6	7.22	532	1.52	0.28	0.94	1.24	0.95	5.90	0.05	0.03	0.05	-9.92	<0.6	-1.6	0.1	0.2
RL-7	200	45.8	RW	32.7	7.00	111	0.46	0.19	0.03	0.14	1.53	0.76	0.05	0.00	0.06	-9.99	0.80	-2.3	-1.8	-4.1
RL-8	100	40.0	RW	20.4	6.01	85	0.29	0.13	0.06	0.08	0.71	0.45	0.08	0.02	0.13	-12.19	2.00	-1.6	-3.4	-7.0
RL-9	150	100.7	NRW	29.5	7.41	412	2.62	0.47	0.11	0.35	1.43	2.46	1.16	0.04	0.20	-10.58	<0.6	-2.2	-0.6	-1.6
RL-11	100	61.1	NRW	21.1	6.75	1999	1.09	0.34	3.97	7.86	0.41	7.71	0.56	0.00	8.69	-11.42	<0.6	-1.2	0.1	0.0
RL-16	18	16.0	RW	22.3	7.42	505	1.38	0.29	0.15	1.46	1.22	4.43	0.14	0.00	0.17	-9.04	<0.6	-2.0	0.1	-0.6
RL-21b	100	85.7	NRW	26.7	7.28	530	1.77	0.45	0.44	1.33	1.62	5.33	0.06	0.03	0.05	-9.82	<0.6	-1.8	0.1	-0.2
RL-23	--	61.2	NRW	29.1	7.10	373	2.24	0.14	0.05	0.61	1.03	3.29	0.16	0.03	0.12	-10.21	<0.6	-1.8	-0.6	-2.1
RL-24	--	110.4	NRW	38.9	7.30	240	1.67	0.16	0.03	0.24	1.26	2.10	0.10	0.01	0.09	-9.69	<0.6	-2.1	-0.8	-2.2
RL-25	100	36.7	RW	22.4	6.67	174	0.49	0.15	0.10	0.42	1.28	1.50	0.07	0.01	0.06	-9.69	<0.6	-1.7	-1.5	-3.6
RL-26	--	61.1	NRW	22.9	7.58	281	1.14	0.21	0.13	0.57	1.04	2.49	0.07	0.02	0.06	-10.54	<0.6	-2.4	-0.3	-1.2
RL-27	100	34.2	NRW	30.4	7.40	470	1.68	0.65	0.30	1.23	1.35	3.64	0.28	0.04	0.34	-9.44	0.80	-2.0	0.1	-0.3
RL-28	200	122.8	NRW	33.7	7.24	498	2.62	0.57	0.26	0.78	1.63	4.12	0.45	0.04	0.33	-9.59	<0.6	-1.8	-0.2	-0.7
RL-31b	--	112.0	NRW	36.1	7.10	422	2.73	0.29	0.07	0.79	1.55	3.70	0.250	0.020	0.260	-9.55	<0.6	-1.9	-0.3	-1.5
RL-34	50	28.0	RW	23.7	6.81	324	0.66	0.19	0.20	1.01	1.02	3.22	0.11	0.07	0.08	-11.28	1.00	-1.5	-0.7	-2.0
RL-36b	150	81.52	NRW	35.9	7.8	372	3.77	0.06	0.05	0.30	0.78	4.01	0.22	0.03	0.10	-9.89	<0.6	-2.4	0.0	-0.5
RL-37	200	114.9	NRW	28.7	7.37	601	3.20	1.87	0.13	0.95	1.44	4.50	0.53	0.04	0.52	-9.01	<0.6	-1.9	0.0	-0.8
RL-38	150	95.4	NRW	29.1	7.44	423	1.40	0.28	0.43	0.88	1.16	4.02	0.09	0.03	0.09	-10.07	<0.6	-2.0	0.0	-0.1
RL-41	100	62.5	NRW	27.4	7.47	432	0.96	0.21	0.65	1.18	1.41	3.97	0.11	0.03	0.23	-10.86	<0.6	-2.1	0.1	0.1
RL-42	--	56.3	NRW	29.7	6.99	526	0.74	0.10	0.56	1.91	0.24	4.87	0.11	0.00	0.35	-9.67	<0.6	-1.5	-0.1	0.5
RL-43	145	101.6	NRW	23.9	7.39	439	1.25	0.26	0.40	1.06	1.26	4.12	0.10	0.04	0.10	-10.28	<0.6	-2.0	0.0	-0.4
RL-46	100	60.8	NRW	25.0	7.41	600	2.04	0.32	0.73	0.99	1.09	4.50	0.74	0.06	0.28	-11.04	0.60	-2.0	0.0	-0.1

Because no pairs of initial and final water wells along a flowpath were identified and given the hydrogeological settings, an alternative modeling approach is proposed for radiocarbon evaluation, where each water sample (recharge and non-recharge) is evolved from pure

water. The basic assumption is that part of the carbon-affecting reactions occur in the unsaturated zone and part in the saturated zone. Soil CO₂ is introduced in the unsaturated zone and since the CO₂ gas concentration in water samples is not known, it was estimated based on thermodynamics, water chemical and physicochemical parameters. The 5% and 95% percentile of calculated CO₂ gas was between 1.0 to 4.0 mmol L⁻¹. Taking into consideration that the vegetation density is relatively scarce during most of the year in the selected sampling sites, the CO₂ gas concentration may be less than 2.5 mmol L⁻¹.

The obtained models for recharge samples were checked manually for reliability (a) by eliminating cases with unrealistic reactions, such as models with unreliable large mass transfers, and (b) by comparing the ¹³C contents of CO₂ gas of the unsaturated zone calculated by mass balance models with literature-derived ranges of values (Mook, 1980; Thorstenson et al., 1983; Phillips et al. 1989; Clark and Fritz, 1997) and excluding balance cases that did not agree with the range of reported ¹³C values. Finally, the ¹⁴C decay equation was applied on geochemical adjusted activity (A_{nd}).

The inclusion of uncertainty limits for analytical chemical and isotopic data is an essential advantage of PHREEQC over other geochemical codes such as NETPATH (Plummer et al., 1991). The solution with data uncertainty makes PHREEQC more robust, because NETPATH may produce large changes in mole transfers in response to small changes in the input data (Parkhurst and Appelo, 1999). PHREEQC's algorithm that allows uncertainty in data is useful in areas with a low density of information on geochemistry, in heterogeneous aquifers, and in areas where potential mixtures of groundwater of different ages exist. The strength of NETPATH is its treatment of isotopic fractionation, compared to the purely mole balance approach of PHREEQC. Isotope fractionation, however, occurs only when carbonates precipitate. If models dissolve only for carbonates, the PHREEQC approach can be used alone.

4. Results and Discussion

Inorganic Chemistry

According to a survey carried out in 2000 (Mahlknecht, 2003), the mineralization of most water samples is low, with specific conductance ranging from 85 to 967 μS/cm. A few

samples located in the Mineral de Pozos area near San Luis de la Paz (Fig. 1) show higher values, in the order of 2000 $\mu\text{S}/\text{cm}$, which is likely due to mixing with water from the deep confined Cretaceous limestone units. The groundwater temperature along basin margins ranges from 17 to 22°C reflecting the mean annual temperature, while groundwater from deeper geological formations reaches a maximum in the order of 40°C. Recharge water from the basin margins is characterized by a low pH, ranging from 6.0 to 6.5, and low DIC on the order of 1.6 mmol L^{-1} . Groundwater from downgradient zones has a pH between 6.5 and 8.8, and a DIC around 4.6 mmol L^{-1} . Groundwater from the recharge zones is predominantly of Ca-HCO₃ facies, and evolving toward a Na-Ca-HCO₃ type water along the groundwater flow system toward discharge areas. A few waters of Ca-SO₄ facies, representing an exception, indicate mixture with groundwater from a deep confined aquifer located in the Mineral de Pozos former mining district in the vicinity of San Luis de la Paz (Fig. 1).

The average alkalinity (as HCO₃) is in the order of 222 mg L^{-1} . Large values of alkalinity (>280 mg L^{-1}) are along the northeastern part of the study area in the vicinities of San Luis de la Paz and San Diego de la Unión, and the southern San Miguel de Allende vicinity. A tendency to lower alkalinity exists toward the western study area. In most samples, groundwater is saturated with respect to calcite.

Stable Isotopes (²H, ¹⁸O) in Groundwater

The stable isotope content of water (¹⁸O and ²H) varies around the median of -10.1‰ and -73.5‰, respectively, with standard deviations of 0.9‰ and 6.4‰, respectively. Groundwater from the eastern part of the basin agrees nicely with the regional meteoric water line (RMWL) developed by Cortés et al. (1997) and fits to the line $\delta^2\text{H} = 8.04 \cdot \delta^{18}\text{O} + 11.84$, while groundwater from the western part shows a distinct regression line ($\delta^2\text{H} = 8.35 \cdot \delta^{18}\text{O} - 16.80$) resulting from a different rainout mechanism and evaporation effects due to farming (Mahlknecht et al., 2004b).

Most groundwater in the valley floor has $\delta^{18}\text{O}$ values between -8 and -10‰, and groundwater throughout the rest of the basin between -12 and -10‰ (Fig. 4). The heavier values coincide with regional discharge zones and the lighter values are characteristic for elevated areas. The areas with the heaviest values are west of Dolores Hidalgo between Rio

Laja and Arroyo El Plan, and along the western side of the Allende dam. The areas with lightest values are observed in the vicinity of San José Iturbide, indicating a likely mountain-front recharge from the Zamorano massif, which is the highest elevation in the region. Other zones with light values are San Luis de la Paz and south of San Felipe. According to this, the water in the lowlands is either lowland recharge with heavier isotopic signature, or it is recharge from rivers fed with lighter upland precipitation that is evaporated to heavier values in the river system. This hypothesis is in agreement with the groundwater flow system.

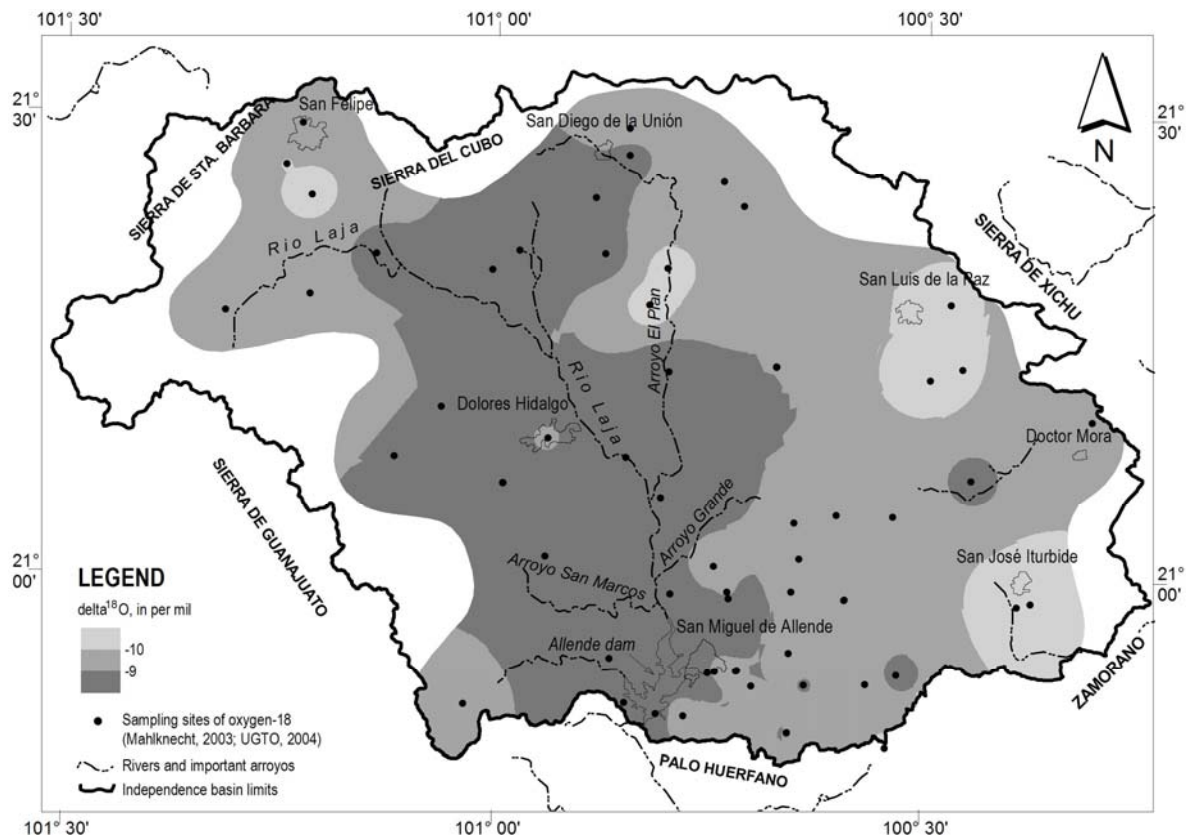


Figure 4: Distribution of $\delta^{18}\text{O}$ groundwater composition in the Independence Basin.

For the water sample results presented in Table 1, the $\delta^{18}\text{O}$ values vary between -12.2 and -9.0 ‰, which indicates that the range of recharge altitudes is relatively small. The lightest values (RL-8, RL-11, RL-34, RL-46) represent infiltration from higher elevation. No age and depth structure is identified with regard to ^{18}O ; and based on the ^{14}C data the $\delta^{18}\text{O}$ of oldest groundwater is similar to modern groundwater indicating that both types of waters

were recharged under similar climatic conditions (Table 1). Due to the low isotopic variability of groundwater in the basin, it is difficult to analyze the sources of groundwater. Thus, additional geochemical data are needed for interpretation.

Hydrochemical Zones and Sources of Water

Hydrochemical zones provide information on plausible recharge sources and groundwater chemical evolution. Different hydrochemical zones were recognized and mapped in the Independence Basin (CEASG, 1999; UGTO, 2004; Mahlkecht et al., 2004a). The hierarchical cluster analysis approach of Mahlkecht et al. (2004a) was selected as starting point and chemical samples from 75 sites and isotopic information from 49 sites (Mahlkecht, 2003; UGTO, 2004) were used to obtain hydrochemical zones. The result was the delineation of 5 zones coinciding more or less with the outlined recharge areas (R₁ to R₅) and one zone in the downgradient non-recharge areas (NR) (Fig. 5).

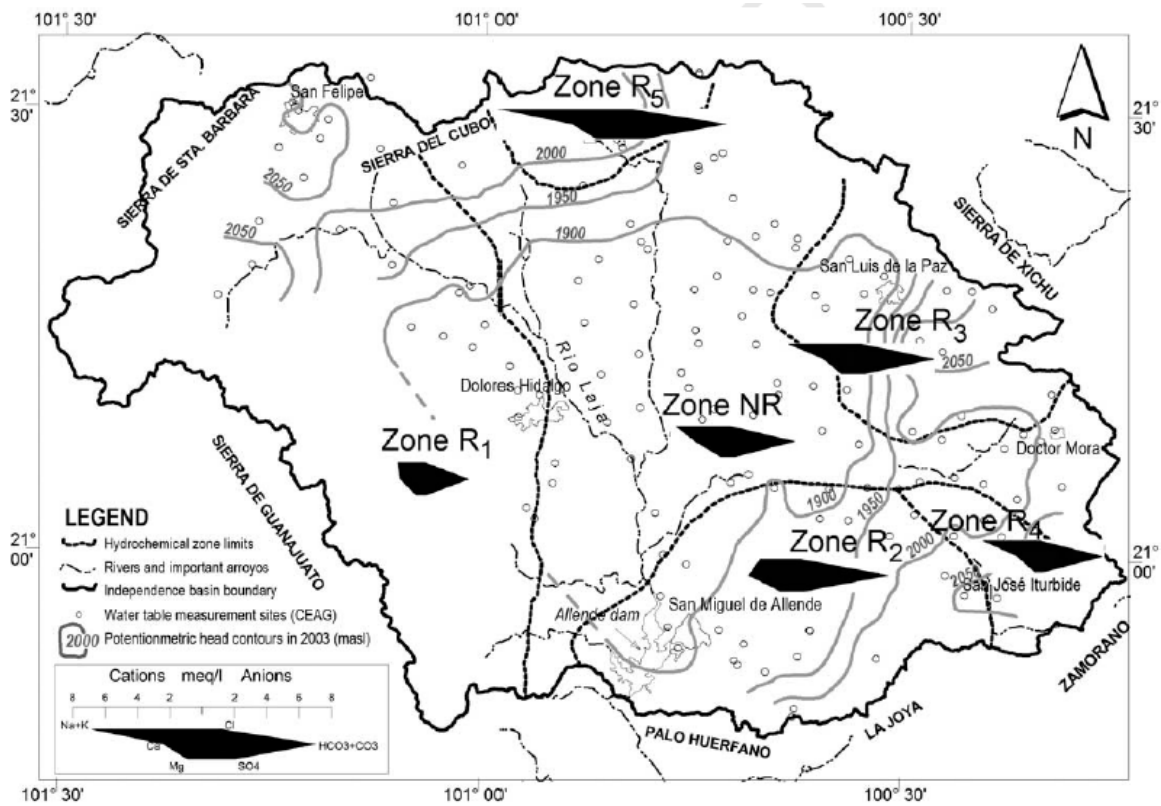


Figure 5: Hydrochemical zones, corresponding Stiff plots, and modern groundwater table configuration of the Independence aquifer system.

The average groundwater chemistry of each hydrochemical zone is presented in Table 2 and in Fig. 5 as Stiff plots. Zone R₁ represents mountain-front recharge along the Sierra de Guanajuato. Zone R₂, located in the San Miguel de Allende area, is mountain-front recharge from the Palo Huerfano and La Joya volcanoes and has relatively high Mg and Ca contents. The high alkali earth content indicates the influence of andesitic rock formations of the contiguous Transmexican Volcano Belt at the southern border of the study area. Zone R₃ is SO₄ and NO₃ affected and coincides with the zones of higher groundwater withdrawals for intensive irrigation in the San Luis de la Paz municipality. Zone R₄ corresponds to a recharge water type and overlaps with zone NR in the downgradient section. Zone NR corresponds to a discharge water type and represents the major hydrochemical zone in the basin. To the north, some groundwater are characterized by high Na, F, HCO₃, SO₄, NO₃ and pH (zone R₅), but have similar properties as water supplies in zone R₃.

Table 2: Mean water chemistry of hydrochemical zones (in mmol L⁻¹).

Zone	Temp (°C)	pH (-)	Cond. (μS/cm)	Na	K	Mg	Ca	SiO ₂	HCO ₃	F	Cl	NO ₃	SO ₄
R ₁	25.1	7.1	284.9	1.10	0.24	0.18	0.62	1.35	2.59	0.02	0.14	0.03	0.10
R ₂	25.5	7.3	538.3	1.73	0.31	0.46	1.33	1.14	5.01	0.04	0.18	0.05	0.20
R ₃	27.5	7.5	587.9	3.27	0.51	0.33	0.84	1.17	4.84	0.13	0.53	0.18	0.37
R ₄	31.7	7.5	411.7	2.88	0.18	0.06	0.56	0.88	3.74	0.08	0.21	0.02	0.18
R ₅	28.7	7.8	950.9	6.47	0.37	0.46	1.21	0.84	7.03	0.15	1.22	0.06	1.02
NR	27.6	7.4	495.6	2.48	0.47	0.14	0.90	1.60	4.13	0.06	0.29	0.03	0.30

The source of water in the zones R₁, R₂, R₃, R₄, and R₅ is mountain-front recharge, while zone NR receives contributions from surface water from the upper Rio Laja and arroyos as suggested earlier by isotopic evidence from lateral inflows and from the upgradient hydrochemical zones.

Carbon (^{13}C , ^{14}C) and Tritium (^3H) Isotopes

Radiocarbon data measured on DIC varies from 19 to 94 pmc. The high values representing recharge conditions are observed in groundwater located in the southern mountain front (San Miguel de Allende and San José Iturbide). ^{14}C activities are lowest in the central part of the basin (Dolores Hidalgo) and southwest from Doctor Mora. The ^{14}C activities generally indicate that waters of the Independence Basin have ages of thousands of years. Tritium is detected only in 3 samples out of 24, with values varying between 0.8 and 2.0 TU (Table 1). The detection of tritium in groundwater is interpreted as an evidence that groundwater contains a contribution of young water. The ^{13}C content of DIC varies between -5.9 and -13.4‰. (Table 5). A trend of decreasing ^{14}C activity associated with a change toward heavier $\delta^{13}\text{C}$ values indicates that geochemical reactions are affecting the ^{14}C concentration along the groundwater flow system. Spatially, a general tendency from lighter to heavier values is recognized from basin's south to the north. The measured ^{13}C content of carbonate minerals varies between -2 and +1.5 ‰.

Supposing an initial value of -18‰ for the soil CO_2 , the enrichment of $\delta^{13}\text{C}$ due to calcite dissolution assuming a $\delta^{13}\text{C}_{\text{calcite}}$ of 0 ‰, could attain values in the order of -9‰. Values enriched over -9‰ can be explained a) by incongruent dissolution of dolomite, i.e. calcite precipitates as dolomite dissolves, and/or b) by lower initial $\delta^{13}\text{C}$ values. The dissolution of dolomite would add carbonate with $\delta^{13}\text{C}$ of around ~0‰ and could be identified by the magnesium excess, i.e. the difference between measured magnesium and magnesium in recharge water. From evaluation of analytical data, however, it is concluded that the magnesium excess is relative low and could not be responsible for $\delta^{13}\text{C}$ values in the order of -5.8‰. This suggests that a lower initial $\delta^{13}\text{C}$ value for the soil CO_2 in the order of -14.5‰ can explain the $\delta^{13}\text{C}$ pattern. The final $\delta^{13}\text{C}_{\text{DIC}}$ values between -5.8 and -10‰ indicate that the initial values for the soil CO_2 could lie in the range of -14 to -17‰, which corresponds to CAM vegetation or a mixture between C_3 (from -24 to -30‰) and C_4 plants (from -10 to -16‰) (Clark and Fritz, 1997). The current vegetation corresponds to hot open ecosystems including cacti, grasslands and maple forests in uncultivated areas and wheat, corn, legumes and other crops in cultivated areas. Relicts of natural vegetation located in the Sierra de Guanajuato indicate grasslands under maple forests, which is congruent with

the savanna-like climate described by Navarro de León et al. (2005) and the observed $\delta^{13}\text{C}$ range.

Initial ^{14}C Activity

The calculation of the radiocarbon age requires an estimation of initial ^{14}C activity, A_0 . From the relationship between ^{14}C and ^{13}C for most samples (Table 5), it is expected that the initial ^{14}C activity corresponds to the time period before nuclear testing in the early 1950's. The atmospheric ^{14}C activity before 1950 shows little variation and is assumed to be 100 pmc (Stuiver et al., 1991; Kalin, 2000). On the other hand, sample RL-16 and RL-34 have relatively high measured ^{14}C activities (86.4 and 84.8 pmc, respectively), as well as enriched $\delta^{13}\text{C}$ values (-9.8 and -10.3‰), indicating that carbonate dissolution already took place. This indicates that the initial ^{14}C activity for these samples was higher than 100 pmc. They are apparently influenced by bomb- ^{14}C that corresponds to the time period between 1953 and 1963 where high neutron fluxes associated with the nuclear devices explosion produced large quantities of ^{14}C , so that by 1964 the atmospheric concentrations in the northern hemisphere have almost doubled (Mook, 1980; Clark and Fritz 1997). As a result, ^{14}C activities in the order of 120 pmc were observed in CO_2 gas samples at the top of the unsaturated zone (Thorstenson et al., 1983). It is assumed that the initial ^{14}C activity for samples RL-16 and RL-34 was 120 pmc. Sample RL-16 is tritium-free but the presence of CFC in recent measurements indicates a component of modern groundwater (UGTO, 2004).

Geochemical Reactants

Groundwater of the basin is undersaturated with respect to albite, anorthite, and chlorite; and between undersaturated and saturated with respect to microcline. According to petrographic investigations, albite is the most common mineral phase (>20 weight-%), followed by orthoclase and microcline. Anorthite weathering is only of local importance (San Miguel de Allende and San Luis de la Paz). The speciation-saturation calculations with PHREEQC indicate that groundwater is between equilibrium and slight supersaturation with respect to silica. Petrographic evidence shows that between 5 and 30 % of the framework is detrital SiO_2 . The relatively high H_4SiO_4 concentration in groundwater (median = 1.0×10^{-3} mmol/L) favors the hypothesis of the presence of

amorphous silica rather than phases like quartz or chalcedony. However, large chalcedony deposits were observed in the outlined discharge zones (Navarro de León et al., 2005) (Fig. 2), suggesting volcanic reactants weathering to chalcedony. The large silica concentrations in groundwater (>60 mg/L) indicate that less stable volcanic minerals are reactive than tuffs, which represent the major groundwater producing zones. Calcite occurs mainly as cement in sandstones and mudstones, and as caliche. Saturation indices of calcite are substantially less than zero for shallow groundwater (< -3.8) near the basin margins, and around zero for deep groundwater (between -0.7 and $+1.0$) in the center and north of the basin. Mineralogical investigations give no evidence of calcite precipitation. The supersaturation in Table 3 is possibly due to degassing processes during the sampling process. Groundwater is undersaturated with respect to gypsum, which is consistent with its absence in many soil samples. Pyrite, an alternative source of dissolved sulfate, is only a negligible component of the Tertiary and Quaternary matrix and not detected in this or any other surveys. Groundwater is oversaturated with respect to kaolinite, which is consistent with the mineralogical occurrence of this mineral. Goethite and hematite are common minerals in sand and mudstones and produce red- and yellow-brown colors. Petrographic studies indicate that hematite is present in all samples. With regard to the cation exchange capacity (CEC) of expandable clays, the range is between 20 and 50 meq/100g in the granular aquifer material and up to 10 meq/100g for the fractured aquifer material. Ca uptake and Na release reaction is by far the most important exchange option (Ornelas-Soto, 2003; UGTO, 2004). Dissolution of carbonate minerals is the main reaction, which can affect the ^{14}C activity in the Independence Basin, while cation exchange (Ca^{2+} for Na^+) permits that the dissolution of carbonate continues.

Table 3: Ranges of mass transfer (in mmol L⁻¹) of PHREEQC mass-balance models in the Independence aquifer. Positive mass transfers add matter to groundwater (dissolution), negative mass transfers subtracts matter from groundwater (precipitation/exsolution).

Reaction	Mass transfers			
	Recharge samples		Non-recharge samples	
	min	max	min	max
CO ₂ gas	1.5	4.1	*	*
Calcite	0.2	2.0	0.0**	0.0
Dolomite	0.08	0.9	0.0	3.8
Gypsum	0.0	0.14	0.03	0.5
Kaolinite	0.02	1.4	-2.9	-0.04
Chalcedony	-0.5	2.4	-7.1	-0.4
K-feldspar	0.04	0.3	-0.05	1.57
Albite	0.2	1.7	0.0	4.3
Ca/Na exchange	0.0	0.6	-1.4	-0.16

* not allowed transfer in non-recharge samples

** models with calcite precipitation excluded

Mass Balance Models

The geochemical mass-balance code PHREEQC (Parkhurst and Appelo, 1999) was used to construct mass-balance models and to investigate the radiocarbon ages of groundwater in the Independence Basin. Phases constraining the geochemical models were calcite, dolomite, kaolinite, silica, gypsum, potassium feldspar, sodic plagioclase, chlorite, and Ca/Na-exchange. Important element transfers (calcite, kaolinite, gypsum) were forced to be present in all mass balance models. Although sulfide mineral oxidation (e.g. pyrite) is theoretically accountable for sulfate in the unsaturated zone, only gypsum was used in the models. The strong relationship between chloride and sulfate and a factor analysis reported in Mahlkecht et al. (2004a) support the hypothesis that gypsum is previously formed by evaporation and may be greatly responsible for the dissolved sulfate in groundwater. In addition, the higher sulfate concentrations in young groundwater coincide with heavy irrigated agricultural areas. Fertilizers may also contribute sulfate and chloride in some areas. The sulfate concentration of older groundwater could be from limestone formations, which probably contain gypsum. Only in thermal waters of the basin's north between San

Diego de la Unión and San Luis de la Paz, the oxidation of arsenic bearing sulfides seem to play a role for dissolved sulfate (Mahlknecht et al., 2004a).

Although Ca-montmorillonite is thought to be a plausible reactive phase, it was not included since its consideration would triple the number of model results, but would not affect radiocarbon ages significantly. For the same reason, it was decided to use sodic plagioclase as source of Na respectively, whereas albite was excluded from models. Thus, models that use sodic plagioclase represent also albite. Likewise, eventual magnesite transfers are represented by the dolomite phase.

A summary of the modeling transfers is presented in Table 3. In recharge samples, CO₂ gas dissolution is the most important reactant (<4.1 mmol L⁻¹), followed by calcite dissolution (<1.9 mmol L⁻¹) and plagioclase weathering (<1.9 mmol L⁻¹). Amorphous silica precipitates (<0.5 mmol L⁻¹) and dissolves along the flow paths (<2.4 mmol L⁻¹). The dissolution of dolomite and gypsum is relatively small (<0.2 mmol L⁻¹). Kaolinite precipitates up to 2.4 mmol L⁻¹. In non-recharge samples, calcite dissolution is insignificant, while dolomite dissolution becomes more important (<3.8 mmol L⁻¹). Amorphous silica precipitation becomes the most important process in down-gradient zones (<7.1 mmol L⁻¹). K-feldspar and plagioclase weathering are the most prominent silicate reactions.

Radiocarbon Ages

The ¹⁴C activities were adjusted for geochemical reactions by using mass balance models between pure water and final well, in order to evaluate the residence time of paleowaters. The basic assumption is that the carbon-affecting reactions occur part in the unsaturated zone and part in the saturated zone. Soil CO₂ is introduced in the unsaturated zone with an isotopic composition of -21‰, which is derived from oxidation of organic carbon (-25‰), adjusted for diffusion (~4‰). The water in equilibrium with this CO₂ is between -18‰ and -13‰ DIC, taking into account fractionation between pH 6 and 7. The assumption is that any CO₂ or carbonate mineral reacting in the unsaturated zone will eventually lead to a value between -13 and -18‰ DIC. Thus, a set of unsaturated zone minerals - calcite and dolomite – are hypothesized that introduce carbon at -15.5 ± 2.5‰ and 100 pmc. In the saturated zone is no additional source of CO₂, and any calcite or dolomite that dissolve, introduce carbon that has a composition of 0‰ and 0 pmc. Thus, the distribution of

carbonate dissolution between unsaturated and saturated zone is used to adjust the ^{13}C of the water and simultaneously calculate A_0 for carbon-14 decay equation. Since carbonates are supposed not to precipitate, it is not necessary to use NETPATH's isotopic fractionation equations.

To the $\delta^{13}\text{C}$ measured on DIC were given uncertainty ranges of $\pm 1\%$ for $\delta^{13}\text{C}_{\text{DIC}}$. The range of $\delta^{13}\text{C}_{\text{carbonates}}$ was -2 to +2‰, which corresponds approximately to the reported measurements. In this way, the range of residence time for each sample includes practically every plausible geochemical uncertainty. Table 4 presents an example of the mass balance modeling results and age estimation.

Fig. 6 shows a plot of the geographical distribution of the radiocarbon residence time. It indicates recharge occurs on the Transmexican Volcano Belt (Palo Huerfano and La Joya) in the south, on the Sierra de Guanajuato in the west, and on San José Iturbide and Doctor Mora municipalities (Zamorano massif) in the southeast. The oldest residence time indicates around ~11 ka, found in the heavily exploited area west of Dolores Hidalgo, which coincides with the modern groundwater movement towards the basin's center (Fig. 2 and 5).

Table 4: Mass transfer results for solution RL-41 (all data are in $\text{mmol L}^{-1} \text{H}_2\text{O}$). Positive values indicate dissolution between initial (pure water) and final water; negative values indicate precipitation. “ $\text{CO}_2(\text{g})$ ” means carbon dioxide gas. “CaX2” and “NaX” indicate the Na for Ca exchange surfaces. “Calcite (100 pmc/0 pmc)” and “Dolomite(100 pmc/0 pmc)” signifies the amount of calcite and dolomite dissolved in the unsaturated (100 pmc)/saturated zone (0 pmc), respectively.

Model No.	Albite	Calcite (100 pmc)	Calcite (0 pmc)	$\text{CO}_2(\text{g})$	Dolomite (100 pmc)	Dolomite (0 pmc)	Gypsum	Halite	Kaolinite	Chalcedony	K-feldspar	CaX2	NaX	A_{nd}	A_0	Age (years)
1	0.33	0.47	1.24	2.27	0.00	0.05	0.10	0.22	-0.20	0.00	0.06	-1.56	3.12	21.95	67.16	9245
2	0.33	0.00	1.71	2.27	0.00	0.05	0.10	0.22	-0.20	0.00	0.06	-1.56	3.12	21.95	55.66	7692
3	0.33	0.37	1.34	2.27	0.05	0.00	0.10	0.22	-0.20	0.00	0.06	-1.56	3.12	21.95	67.16	9245
4	0.33	0.00	1.71	2.27	0.05	0.00	0.10	0.22	-0.20	0.00	0.06	-1.56	3.12	21.95	58.11	8048
5	1.07	0.00	1.34	2.64	0.05	0.00	0.10	0.22	-0.56	-1.48	0.06	-1.19	2.38	21.95	67.16	9245
6	1.27	0.00	1.24	2.74	0.00	0.05	0.10	0.22	-0.66	-1.88	0.06	-1.09	2.18	21.95	67.16	9245

Table 5: Carbon isotope data and radiocarbon residence time estimation of uncorrected data and according to the PHREEQC mass balance approaches.

ID	$\delta^{13}\text{C}$ (‰ VPDB)	A_t (pmc)	$A_{\text{CO}_2(\text{g})}$ (pmc)	uncorrected (years)	PHREEQC mass-balance model		
					minimum (years)	median (years)	maximum (years)
RL-9	-7.18	34.96	100	8,700	--	5,400	--
RL-16	-9.77	86.44	120	2,700	recent	recent	recent
RL-21	-10.72	62.47	100	3,900	recent	1,400	2,700
RL-24	-9.28	29.03	100	10,200	7,000	7,100	7,100
RL-25	-13.44	94.28	100	500	recent	recent	recent
RL-26	-11.77	44.08	100	6,800	2,800	4,500	5,900
RL-27	-5.87	24.32	100	11,700	--	7,600	--
RL-28	-7.20	29.77	100	10,000	--	6,300	--
RL-31	-9.05	27.57	100	10,700	7,100	7,300	7,600
RL-34	-10.34	84.77	120	2,900	recent	recent	400
RL-36	-10.41	21.95	100	12,500	7,700	9,200	9,200
RL-37	-7.94	18.84	100	13,800	--	10,800	--
RL-38	-8.99	59.14	100	4,300	100	2,500	2,500
RL-41	-10.17	55.58	100	4,900	800	1,400	3,800
RL-43	-10.56	69.38	100	3,000	recent	500	1,900
RL-46	-9.62	65.53	100	3,500	recent	recent	2,000

Groundwater Flow

Predevelopment water levels (pre-1940) indicate that the groundwater flow system in the basin is gravity-driven i.e. recharge areas in the mountains and discharge in the valley-floor (Fig. 2 and 3). According to Navarro de León et al. (2005), the predevelopment flow regime consists of: a) the mountainous area and the borders of the plain with cold springs and phreatophytes; (b) the central plain where lagoons, bogs, saline soils and phreatophytes were abundant; and (c) the area located from the basin center to the basin outlet with the occurrence of chalcedony deposits along with thermalism and artesian phenomena. The three areas correspond to a gravity-driven flow system of local, intermediate and regional order, respectively.

The predevelopment and current water table configurations indicate that the recharge areas remained unchanged during the last decades. Below the 2,000m-contour line, however, the hydraulic gradient has increased due to gradually increasing water extraction. The predevelopment groundwater configuration in Fig. 2 shows a concentric flow from the

recharge areas at the border to the basin center and then to the south according to the surface water drainage pattern. The modern regional groundwater table in Fig. 5 reveals a shift of the regional discharge zone from the south (San Miguel de Allende area) to the basin center (Dolores Hidalgo), which corresponds to a flow inversion in the south (Fig. 5). In addition, the discharge area is extending towards the western study area addressed to the exhaustive groundwater mining due to irrigation in the so-called Laguna Seca (eastern part of the basin).

Although the geochemical and isotopic investigations are roughly consistent with the general flow concept generated by hydraulic-head distribution, there are some discrepancies with both the predevelopment and the current hydraulic-head configuration.

First, the conservative tracer chloride and the specific conductance indicate a tendency of short to longer residence time from southwest (hydrochemical zone R₁) to northeast (hydrochemical zones R₃ and R₅) of the basin (Fig. 5). On the other hand, the calcite saturation index implies undersaturated conditions in zone R₁, R₂, R₄ and R₅, and saturated conditions for the rest of the basin area. The pattern contrasts with the water table configuration, where zone R₃ and R₅ are outlined as recharge formation areas. This observation points out that the northern basin area is not an important recharge area.

Second, the radiocarbon residence time distribution (Fig. 6) matches rather the modern (Fig. 5) than the predevelopment flow configuration (Fig. 2). This divergence between predevelopment conditions and geochemical interpretation is likely due to the fact that the geochemical tracer content in groundwater is gradually modified due to heavy water extraction. Similar observations of transient geochemical conditions in heavy exploited aquifers of semiarid and arid regions have been recently documented in other basins (e.g. Plummer et al., 2004). The knowledge that geochemical tracers do rather reflect transitory than steady-state conditions prior to aquifer exploitation has an important implication on the groundwater modeling procedure, where tracers are used for model calibration.

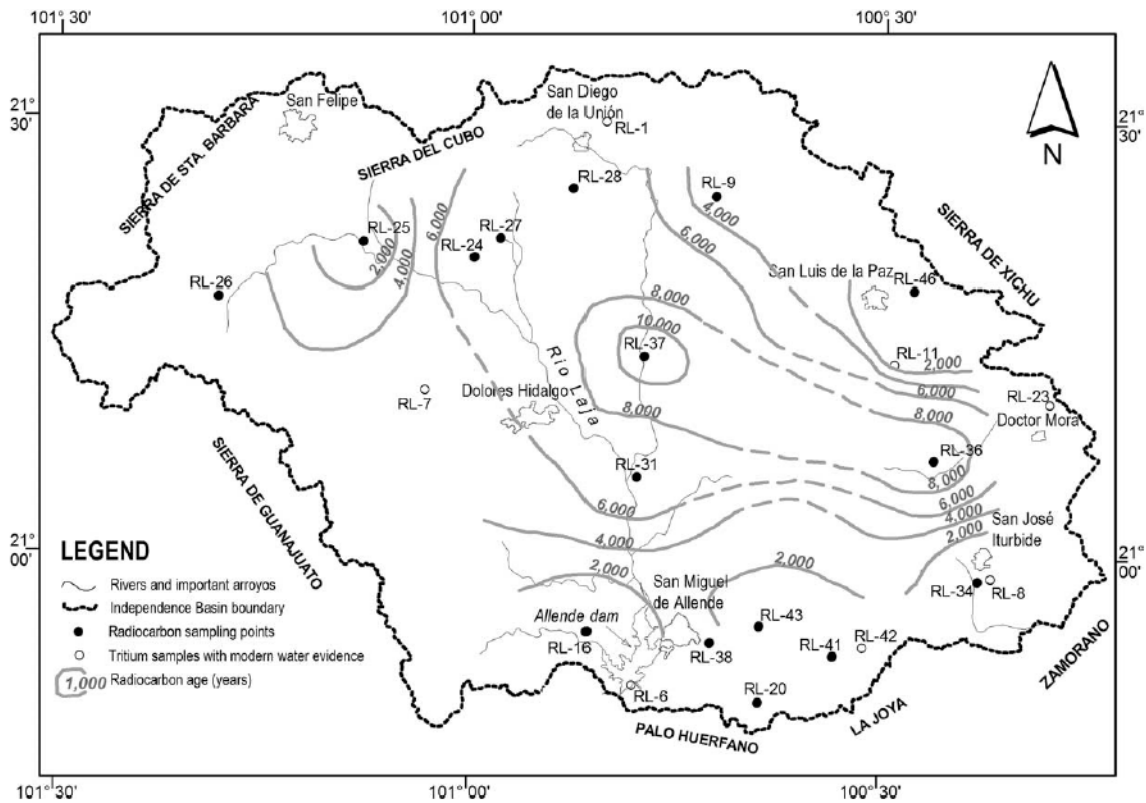


Figure 6: Distribution of radiocarbon residence time (in years).

Finally, recent studies showed that the mass balance approach in some cases in carbonate and calcareously cemented sand aquifers may lead to an overestimation due to transport delays of ^{14}C without significant $\delta^{13}\text{C}$ changes (Maloszewski and Zuber, 1991), the influence of isotope exchange (Aeschbach-Hertig, 2002), and equilibrium dissolution-precipitation assumptions (Gonfiantini and Zuppi, 2003). The influence of these processes on radiocarbon dating are difficult to estimate (Zuber et al., 2004) but is less important in siliceous aquifers such as the present one. The influence of diffusive exchange between aquifer and aquitards may also overestimate the ^{14}C age (Sudicky and Frind, 1981), is however insignificant due to the large thickness of the Independence Aquifer. Nonetheless, it is important to emphasize that geochemical models may be reasonable but not exact correction methods.

5. Conclusion and Recommendation

Environmental isotopes and geochemistry were compared to hydraulic data, in order to understand the dynamics of the groundwater flow system in the Independence Basin in central Mexico. The main conclusions are:

1. The groundwater in the mainly siliciclastic aquifer is characterized by low salinity and the main reactions, that control the geochemical evolution along the groundwater flow systems, are: CO₂ gas dissolution, carbonate dissolution, plagioclase/albite weathering, kaolinite and silica precipitation. The sampled wells and springs from recent studies could be grouped into hydrochemical zones. The isotopic composition of groundwater helped to delineate 6 hydrochemical zones and corresponding recharge sources.
2. The identified primary recharge sources are: a) mountain-front along the west (Sierra de Guanajuato) and south (Palo Huerfano and La Joya) and southeast (Zamorano), and b) vertical upward flow of saline water in the northeast (between San Luis de la Paz and San Diego de la Unión). The mountain-front recharge has an age between 2 and 5 ka, while recharge water from the Zamorano area is up to 9 ka old. The observed groundwater in the basin center is ~11 ka.
3. The hydraulic and geochemical data show that the principal flow pattern for predeveloped and modern conditions in the Independence Basin is concentric starting from basin margins. In the predeveloped state, groundwater flows through the south near the Allende dam coinciding with the surface drainage pattern, while in the present the heavy exploitation provokes discharge toward the basin center and consequently flow inversion in the southern part. Geochemical data match this tendency. Although the hydraulic heads indicate mountain-front recharge in the north and northeast, the geochemical tracers imply no significant recharge entering from these zones.
4. This study demonstrates the importance of using geochemical tracers in hydrological studies. The results of this study - residence time estimation and hydrochemical zone delineation - should be used not only to conceptualize, but also to calibrate groundwater flow models of the Independence Aquifer, in order to develop and refine groundwater management plans and to extract appropriate groundwater volumes aiming to obtain a safe aquifer yield.

5. In order to prevent further water quality deterioration it is necessary to restrict water extractions in the northern basin area (San Diego de la Unión and San Luis de la Paz) and to explore instead new groundwater resources in recharge areas of the southern basin area.

Acknowledgements

The University of Agricultural and Life Sciences (Universität für Bodenkultur Wien, BOKU Wien), Vienna, Austria is thanked for the grants given to Jürgen Mahlkecht. Access to relevant studies have been facilitated by the Comisión Estatal del Agua de Guanajuato (CEAG). Assistance in the field sampling by Gabriela Segura and Markus Gmeindl is greatly acknowledged. Thanks are also due to Lorenz Eichinger for facilitating the tritium analyses. Special thanks to Bruce Davison for the review of the first version of the manuscript. Some of the analytical results used in this paper were obtained during the investigation project contract no. 02/16-CEAG/SDA/CONCyTEG-064, co-funded by CEAG, Consejo de Ciencia y Tecnología de Guanajuato (CONCyTEG) and Secretaría de Desarrollo Agropecuario (SDA). Gian Maria Zuppi and an anonymous reviewer greatly contributed to the improvement of the final version of the manuscript.

References

- Aeschbach-Hertig, W., Stute, M., Clark, J., Reuter, R., Schlosser, P., 2002. A paleotemperature record derived from noble gases in groundwater of the Aquia Aquifer (Maryland, USA). *Geochim. Cosmochim. Acta* 66: 797-817.
- Alanis-Ruiz, E., 2002. Evolución geológica de la Cuenca de la Independencia y sus alrededores, Estado de Guanajuato, México [Geologic evolution of the Independence basin and its surroundings]. B.th. Facultad de Ingeniería, Universidad Nacional Autónoma de México, Mexico, 96 pp.
- Aranda-Gómez, J.J., McDowell, F.W., 1997. Extensión temprana en la porción meridional de la provincia de Cuencas y Sierras de México: basculamiento contemporáneo al depósito de la secuencia terciaria (Eoceno-Oligoceno) del Distrito Minero de Guanajuato [Early extension in the meridional portion of the Basin and Range province of Mexico: contemporary scaling to the tertiary sequence deposit (Eocen-Oligocen) of the Guanajuato mining district]. In: *Proc GEOS. Annual meeting of the Unión Geofísica Mexicana* 17(4): 225-226.
- CEAG, 2001. Piezometría Río Laja – San Felipe, Laguna Seca. Lluvias y Secas; September 1997 – November 2000 [Piezometry of Río Laja-San Felipe, Laguna Seca. Rain and Dry seasons; September 1997 – November 2000]. Comisión Estatal del Agua de Guanajuato, Guanajuato, Mexico.
- CEASG, 1999. Estudio hidrogeológico y modelo matemático del Acuífero del Río Laja-San Felipe [A hydrogeological Study and mathematical model of the Río Laja-San Felipe aquifer]. Prof. Rep., Comisión Estatal del Agua y Saneamiento de Guanajuato, Mexico (Contract no. CEAS-APA-GTO-98-002).

Mahlknecht et al., 2006. *J. Hydrol.*

- CEASG, 2000a. Seguimiento del estudio hidrogeológico y modelo matemático del acuífero del Valle de Laguna Seca, Gto. (Sinopsis). [Update of the hydrogeological study and mathematical model of the Laguna Seca aquifer. Synopsis]. Comisión Estatal de Agua y Saneamiento de Guanajuato, Guanajuato, Mexico.
- CEASG, 2000b. Seguimiento del estudio hidrogeológico y modelo matemático del acuífero Río Laja – San Felipe, Gto. (Sinopsis). [Update of the hydrogeological study and mathematical model of the Río Laja – San Felipe aquifer. Synopsis]. Comisión Estatal de Agua y Saneamiento de Guanajuato, Guanajuato, Mexico.
- Cerca-Martínez, L.M., Aguirre-Díaz, G.J., López-Martínez, M., 2000. The geological evolution of southern Sierra de Guanajuato; a documented example of the transition from the Sierra Madre Occidental to the Mexican Volcano Belt. *International Geology Review*, v.42, p. 131-151.
- Clark I.D., Fritz, P., 1997. *Environmental isotopes in hydrogeology*. Lewis Publishers, New York, USA: 329 pp.
- CNA, 1992. Diagnóstico de las condiciones geohidrológicas actuales y de las alternativas de operación del acuífero de la cuenca alta del Río Laja, Estado de Guanajuato [Diagnostics of the actual geohydrological conditions and operation alternatives of the Cuenca Alta del Río Laja Aquifer, Guanajuato State]. Comisión Nacional del Agua, Mexico.
- Cortés A., Durazo J., Farvolden R. (1997) Studies of isotopic hydrology of the Basin of Mexico and the vicinity: annotated bibliography and interpretation. *J. Hydrol.* 198: 346–376.
- Eguiluz de Antuñando, S., Aranda-García, M., Marret, R., 2000. Tectónica de la Sierra Madre Oriental [Tectonics of the the Sierra Madre Oriental]. *Boletín de la Sociedad Geológica Mexicana* 53: 1-26.
- Gonfiantini, R., Zuppi G.M., 2003. Carbon exchange rate of DIC in karst groundwater. *Chem. Geol.* 197: 319-336.
- IMTA, 1999. ERIC II: Climatic database of Mexico (compact disc). Instituto Mexicano de Tecnología del Agua, Cuernavaca.
- Kalin R.M., 2000. Radiocarbon dating of groundwater systems. In: Cook P.G., Herczeg A.L. (eds.) *Environmental tracers in subsurface hydrology*. Kluwer, Dordrecht, pp 111–144.
- Mahlknecht, J., 2003. Estimation of recharge in the Independence aquifer, central Mexico, by combining geochemical and groundwater flow models. PhD thesis, Institute of Applied Geology, University of Agricultural and Life Sciences (BOKU) Vienna, Austria, 296 pp.
- Mahlknecht, J., Steinich, B., Navarro de León, I., 2004a. Groundwater chemistry and mass transfers in the Independence aquifer, central Mexico, by using multivariate statistics and mass-balance models. *Environ. Geol.* 45(6): 781-795.
- Mahlknecht, J., Schneider, J.F., Broder, J.M., Navarro de León, I., Bernasconi, S.M., 2004b. Groundwater recharge in a sedimentary basin in semi-arid Mexico. *Hydrogeol. J.* 12 (5): 511-530.
- Maloszewski, P., Zuber, A., 1991. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate rocks. *Water Resour. Res.* 27, 1937-1945.
- Martínez-Reyes, J., 1992. Mapa geológico de la Sierra de Guanajuato, con resumen de la geología de la Sierra de Guanajuato [Geological map of the Sierra de Guanajuato, with summary] (scale 1:100,000). *Geological and Mine maps* 8.
- Mook, W.G., 1980. Carbon-14 in hydrogeological studies. In: Fritz P, Fontes JC (eds) *Handbook of environmental isotope geochemistry. The terrestrial environment, A*, v.1. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands: 49-74.
- Navarro de León, I., 2005. Análisis de estrategia del manejo integrado de agua subterránea mediante modelación del flujo: Cuenca de la Independencia, Guanajuato, México [Analysis of integrated groundwater management strategy using flow modeling: Independence Basin, Guanajuato, Mexico.] PhD thesis. Universidad Autónoma de Nuevo León, Mexico.

- Navarro de León, I., Garfias-Soliz, J., Mahlkecht, J., 2005. Groundwater flow regime under natural conditions as inferred from evidence and field observations in a semi-arid basin: Cuenca de la Independencia, Guanajuato, México. J. Arid Environ. (accepted).
- Nieto-Samaniego, A.F., Macias-Romo, C., Alaniz-Alvarez S.A., 1996. Nuevas edades isotópicas de la cubierta volcánica cenozoica de la parte meridional de la Mesa Central, México [New isotopic ages of the volcanic cenozoic cover of the meridional Mesa Central, Mexico]. Universidad Nacional Autónoma de México, Instituto de Geología, Revista Mexicana de Ciencias Geológicas 13: 117-1226.
- Ornelas-Soto N., 2003. Caracterización de la química y mineralogía de suelos y rocas en la zona de San Miguel de Allende [Chemical and mineralogical characterization of soils and rocks in the San Miguel de Allende zone]. B thesis, Centro de Investigación en Química Inorgánica, Universidad de Guanajuato.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geol. Surv. Wat.-Resour. Inv. Rep. 99-4259: 310 pp.
- Pérez-Venzor, J.A., Aranda-Gómez, J.J., Mc Dowell, F., Solorio-Munguía, J.G., 1996. Geología del Volcán Palo Huérfano, Guanajuato, México [Geology of Palo Huerfano volcano, Guanajuato, Mexico]. Universidad Nacional Autónoma de México, Instituto de Geología, Revista de Ciencias Geológicas 13(2): 174-183.
- Phillips, F.M., Tansey M.K., Peeters L.A., Cheng, S., Long, A., 1989. An isotopic investigation of groundwater in the Central San Juan Basin, New Mexico: Carbon-14 dating as a basis for numerical flow modeling. Water Resour. Res. 25: 2259-2273.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991. An interactive code (NETPATH) for modeling net geochemical reactions along a flow path. U.S. Geol. Surv. Wat.-Res. Invest. 91-4078.
- Plummer, L. N., Bexfield, L. M., Anderholm S.K., Ward E.S., Busenberg, E., 2004. Hydrochemical tracers in the middle Rio Grande Basin, USA: 1. Conceptualization of groundwater flow Hydrogeology Journal 12:359-388.
- Ramos-Ramírez, E., Guzmán-Andrade, J.J., Sandoval-Juárez, M.C., Gallaga-Ortega, Y., 2002. Caracterización de Arcillas del Estado de Guanajuato y su Potencial Aplicación en Cerámica [Characterization of clays from Guanajuato state and its potential application in ceramics]. Universidad de Guanajuato, Acta Universitaria 12(1): pp. 23-30.
- SAGAR, 1999. Anuario estadístico de la producción agrícola de los Estados Unidos Mexicanos, 1998 [Statistical handbook of the agricultural production in Mexico, 1998]. Secretaría de Agricultura, Ganadería y Recursos Hidráulicos México, D.F. 308 pp.
- SARH, 1972. Estudio geohidrológico de la Cuenca Grande del Río Laja, Guanajuato [Geohydrologic study of the Great Rio Laja Basin]. Contract No.: EI-71-35, AS-95. Secretaría de Recursos Hidráulicos, Mexico D.F., Mexico.
- SARH, 1986. Actualización de las condiciones piezométricas en las zonas de Abasolo, Cuenca Grande del Río Laja y Silao-Romita, estado de Guanajuato. [Actualization of piezometric conditions in the Abasolo, zones, Great Rio Laja Basin. Contract No. B-76-1986. Secretaría de Recursos Hidráulicos, Mexico D.F., Mexico.
- SARH, 1992. Diagnóstico de las condiciones geohidrológicas actuales y de las alternativas de operación del acuífero de la Cuenca Alta del Río Laja, estado de Guanajuato [Diagnostics of the current geohydrologic conditions and management alternatives of the Great Rio Laja aquifer. Secretaría de Recursos Hidráulicos, Mexico D.F., Mexico.
- Sudicky, F.A., Frind, E.Q., 1981. Carbon-14 dating of groundwater in confined aquifers: implications of aquitard diffusion. Water Resour. Res. 17: 1060-1064.
- Stuiver, M., Braziunas, T.F., Becker, B., Kromer B., 1991. Climatic, solar oceanic and geomagnetic influences on the late-glacial and Holocene atmospheric $^{14}\text{C}/^{12}\text{C}$ change. Quat. Res. 35: 1-24.

Mahlknecht et al., 2006. J. Hydrol.

Thorntenson, D.C., Weeks, E.P., Hass, H., Fisher, D.W., 1983. Distribution of gaseous $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, $^{14}\text{CO}_2$ in the sub-soil unsaturated zone of western U.S. Great Plains: Radiocarbon 25: 315-346.

UGTO, 2004. El impacto de un entorno complejo y transitorio para el agua subterránea - Una investigación hidrogeológica y geoquímica en la zona de San Miguel de Allende [The impact of a complex and transient system for groundwater – a hydrogeological and geochemical research in the San Miguel de Allende zone]. Prof. Rep., Contract No. 02/16-CEAG/SDA/CONCYTEG-064. Facultad de Ingeniería de Geomática de Hidráulica, Universidad de Guanajuato.

Vasallo, L.F., Martínez-Reyes, J., Pierre-Paris, J., 1996. Estructuras Circulares y lineales en el distrito minero de Guanajuato, México y su significado en la prospección minera. Universidad Nacional Autónoma de México [Circular and linear structures in the Guanajuato mining district], Instituto de Geología, Revista Mexicana de Ciencias Geológicas 13(2): 252-257.

Zuber A., Weise S.M., Motyka J., Osenbrück K., Rózanski K. (2004) Age and flow pattern of groundwater in a Jurassic limestone aquifer and related Tertiary sands derived from combined isotope, noble gas and chemical data. J. Hydrol. 286: 87-112.