



Hydrogeological and hydrochemical characterization of two karstic discharge areas in San Luis Potosí, Mexico

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Abstract

Two karstic discharge areas, Río Verde (RV) and Ciénega de Cabezas (CC), located in a distance of 80 km to each other are chosen to determine the influence of local variations in geology and climatic condition on water chemistry and to examine if the groundwater, supplying the discharge areas, undergoes the same evolution and has a common source. Both study areas are situated on the carbonate platform Valles-San Luis Potosí and comprise a similar geological setting, but despite of their spatial vicinity the climate is semiarid in RV and humid in CC presenting an important factor on the amount of discharge and the concentrations of ions in the discharge. The investigation encompasses discharge, hydrochemical and physico-chemical parameter evaluations as well as the determination of saturation indices, hydrochemical modelling and water type characterization of surface water samples to derive knowledge of the groundwater systems. Scatterplots and saturation indices were used to proof the influence of lithological variability. Both study areas represent normal alkaline water, marked by high concentrations of calcium and magnesium with varying concentrations of bicarbonate and sulphate. In RV, the water interacts with dolomite rocks and gypsum layers, whereas in CC the dolomite content is depleted and the influence of limestone rocks increases. The climatic impact on the groundwater in RV is noticeable by the increase in ionic concentrations due to higher evaporation. In CC the higher amount of precipitation dilutes the groundwater and causes decreasing ionic concentrations.

Keywords karst aquifers · Hydrogeochemistry · Discharge measurements · Valles-San Luis Potosí

Introduction

Karst aquifers

Karst aquifers are important georesources with essential functions regarding groundwater distribution and water supply around the world. Due to the complex structure and

characteristics of karst aquifers, such as high flow and percolation rates as well as turbulent flow conditions caused by the diversity of fractures and caverns (Toran et al. 2007), the approved measuring methods for non-karst conditions like borehole pumping tests and contaminant distribution models are mostly not applicable (Bakalowicz 2005). Therefore, alternative methods are preferred, such as hydrochemical and isotopic investigations (Mahlknecht et al. 2006). Also tests with natural and anthropogenic tracers are adequate to determine characteristics of karst aquifers (Land 2005). Several studies on the characterization of karst aquifers were conducted in areas throughout the world. For example, studies in the Tunesian Chott's region on hydrogeochemical characterization of groundwaters (Kamel et al. 2008), hydrochemical variation in the spring water between Jerusalem–Ramallah Mountains and Jericho Fault, Palestine (Khayat et al. 2009), and the relative importance and chemical effects of diffuse and focused recharge in an eogenetic karst aquifer from the unconfined upper Floridan aquifer, USA (Ritorto et al. 2009).

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Mexico comprises five carbonate rock provinces (Fig. 1) mostly associated with the mountain range Sierra Madre Oriental in the north-eastern part of the country including the Coahuila Platform, the Mexican fold-and-thrust belt and the Valles-San Luis Potosí Platform (PVSLP). Two provinces are not connected to the mountain range: the Morelos Platform in the south of Mexico City and the Yucatán Platform. These five carbonate rock provinces except one, the Yucatán Platform, are of Mesozoic age and consist of tightly folded marine sediments, comprising regional karstic aquifers (Ortega-Gutiérrez et al. 1992). The unfolded Yucatán Platform is much younger and of Eocene to Quaternary age.

In order to transfer and verify the knowledge from above-mentioned studies and to understand the water characteristics of karst aquifers in the PVSLP, the regions Río Verde (RV) and Ciénega de Cabezas (CC) were chosen. The aim of the investigation is to study the contrasting hydrochemical characteristics of two discharge areas to derive knowledge of the groundwater flow paths and possible water–rock interactions.

Investigation area: geography and climate

The study area RV comprises two separated sampling areas (Fig. 2b, c), which are summarized to one since the climatic condition is very similar with a semiarid climate on an altitude of 1000 to 1200 m asl. Available groundwater contour maps for 2006 and 2007 (CONAGUA 2015a, b) indicate a prevailing flow regime from the western mountain ranges

to the plateau in south-eastern direction (at the city Villa Juárez), whereas drawdown cones are recognized at the city RV and are controlled by pumping well areal distribution (Fig. 3). The region CC is located 80 km in south-eastern direction, where on an altitude of around 250 m asl. a humid climate prevails. Since there are no wells in this area, no groundwater contour map is available for this region. The dry climate with summer rains of RV (average of 480 mm a^{-1} ; Rocha-Escalante 2009) reaches temperatures up to 40° C in spring/summer and 21° C during winter averaged within the period 1980–2004. The area CC is characterized by a warm climate with an average annual temperature of 24° C ; maximum temperature is around 37° C in May and June and minimum temperature around 13° C in January. The average annual rainfall amounts to 1466 mm, whereas March represents the month with least (20 mm) and September with highest precipitation (336 mm) (Torres 2008). Both areas belong to the Pánuco river basin, draining the east-central part of the state San Luis Potosí into the Gulf of Mexico. Several natural groundwater discharges are found in RV, water budget calculations indicate a total runoff of about $190 \times 10^{-6} \text{ m}^3 \text{ a}^{-1}$ (Rocha-Escalante 2009). This discharge volume coincides with calculations of the water authority stating a discharge of $186 \times 10^{-6} \text{ m}^3 \text{ a}^{-1}$ (CONAGUA 2015a, b). The discharge area CC is very important comprising several rivers and streams; however, neither calculations nor measurements are available (Torres 2008). The middle and northern sectors of CC are characterized as marsh land, situated in a large karst depression.



Fig. 1 Distribution of the five main carbonate rock provinces of Mexico (modified after Ortega-Gutiérrez et al. 1992)

Investigation area: geology, lithology and hydrogeology

The study areas are situated in the Physiographic Province of the Sierra Madre Oriental on the PVSLP, which is composed of Mesozoic marine sedimentary rocks, limestones and shales (Cretaceous). The Oligocene is represented by rhyolites, andesites, and basalts. Late Miocene to Pliocene terrigenous units crop out, and the Quaternary units consist of basalt, conglomerate and topmost alluvial deposits of streams, composed mainly of gravel and sand (Fig. 4). The main lithologies of the study areas, located on the central part of the PVSLP (Figs. 4, 5), are the Guaxcamá Fm, El Abra Fm, Tamasopo Fm, and Cárdenas Fm (Lower to Upper Cretaceous). Regarding the stratigraphic sequence and the lithology, the Guaxcamá Fm (Aptian) is composed of a thin-layered evaporitic sequence of gypsum and anhydrite, interbedded with few clay and dolomite layers deposited in a low energy marine environment. The thickness is stated to be 520 m, but the lower contact is not entirely known (Planer-Friedrich 2000). The Fm is overlain by the El Abra Fm (Albian-Cenomanian), which is a calcareous complex with a thickness of over 1500 m, built of dark grey reef limestones divided into three facies: forereef, reef and backreef facies. These facies are equivalent to the Tamabra Fm, Taninul Fm and El Abra Fm (Carrillo-Bravo 1971). The Tamabra Fm is a compact dark limestone with thin layers of flintstones. According to López-Doncel (2003) mudstones and wackstones prevail, which intercalate with allochthon sediments (packstones and grainstones with bioclasts). The Taninul Fm is a compact greyish limestone comprising fossils in a fine matrix. The El Abra Fm consists of calcarenites and calclutites as well as units of dolomites and partially dolomitized calcite. The Fm El Abra is related with the Tamaulipas Fm. The Tamasopo Fm (Lower Turonian-Senonian) overlays discordantly the El Abra Fm and is built up of limestones of deep marine environment. The thickness of this microfossil-rich platform varies between 300 and 400 m (Basanez-Loyola et al. 1993; López-Doncel 2003). The Cárdenas Fm (Campanian-Maastrichtian) is classified as lutites alternating with calcareous sandstones and calcarenites (Carrillo-Bravo (1971).

Regarding the permeability of these Fm, the Guaxcamá Fm is classified as low permeable, whereas the El Abra Fm and Tamasopo Fm present secondary permeability due to karstification (Planer-Friedrich 2000). Since the Cárdenas Fm contains lutites and sandstones, the permeability is assumed to be intermediate with hydraulic pathways through fractures.

While the RV study area is situated in the mid of the PVSLP, CC is located next to the border to the oriental fringe (Fig. 5), where further calcareous units crop out. The Tamaulipas Inferior is the lowest unit of cretaceous age and

consists of a cryptocrystalline limestone, which is separated by the Otates Fm, a thin laminated clayey limestone (Carrillo 1961), from the Tamaulipas Superior, a compact fine-grained limestone (Muir 1936). In this part, also the El Abra Fm and Tamabra Fm are present (Aguayo-Camargo 1998). The Agua Nueva Fm is a clayey limestone with lenses of flintstones (Carrillo-Bravo 1971), which is overlain by a fine-grained limestone with intercalations of greyish lutites (San Felipe Fm). The Méndez Fm is the topmost Cretaceous unit built of lutites and clayey limestones.

The western fringe of the PVSLP is built similar to the central part of the PVSLP (Figs. 4, 5), though, the presence of the Tamabra Fm, the forereef facies of the El Abra Fm, prevails overlaying the Guaxcamá Fm. Subsequently, the Soyatal Fm was deposited, bioclastic calcarenites and calclutites (Carrillo-Bravo 1971). Also in this part, the Cárdenas Fm is the topmost cretaceous unit.

Lithological and structural features of the rocks indicate a complex geological history of the PVSLP and the adjacent Mesozoic basin: The Laramide Orogeny, coupled with volcanic activity, developed a horst and graben structure with NE-SW striking faults. This has been modified through weathering, erosion, and karstification, the latter being the most important factor for the development of the hydrogeological characteristics of the dominating carbonate rocks (Carrillo-Bravo 1971).

To understand regional groundwater flow Weyer and Ellis (2015) established a 2D vertical steady-state numerical model based on the topographical surface, the geologic structure and associated estimated permeabilities. The authors applied the model on the eastern part of San Luis Potosí basin to the Atlantic coast. The results show flow patterns indicating a regional connection between topographical higher located recharge areas with lower areas as the San Luis Potosí region with the RV and CC area (Fig. 6).

Methods

Field work included the selection of 51 sites (31 in RV and 20 in CC; Fig. 2 and Table 1) for hydrochemical determination of 28 surface water samples as well as 37 discharge measurements (springs, streams, and channels) during a two week measuring campaign in August 2010. Water sampling was directed to evaluate known karstic natural discharges. The parameters pH, specific electrical conductivity (eC), dissolved oxygen (Ox), water temperature (T) as well as alkalinity are determined in field. For alkalinity determination of filtered water samples, the GRAN-Titration was performed on-site with a Digital Titrator (Hach). Water samples were filtered (0.45 µm) and collected in double acid, low density polyethylene bottles. For stabilization of the cations and trace elements in solution, ultrapure HNO₃ (1%) was

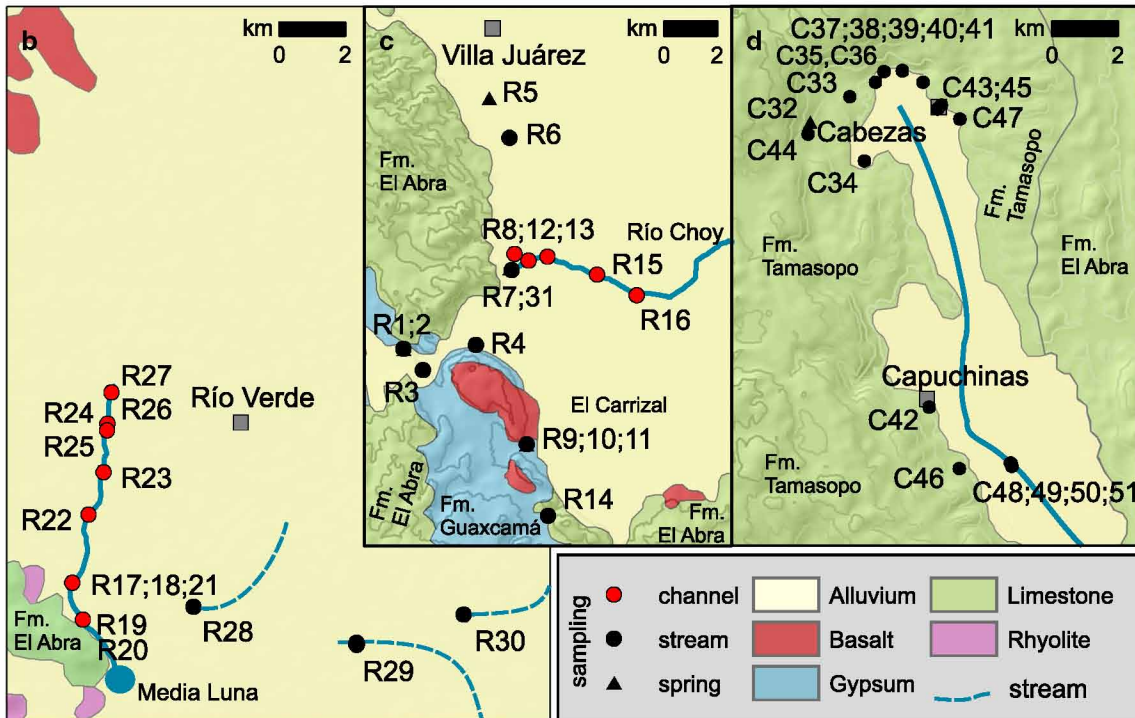
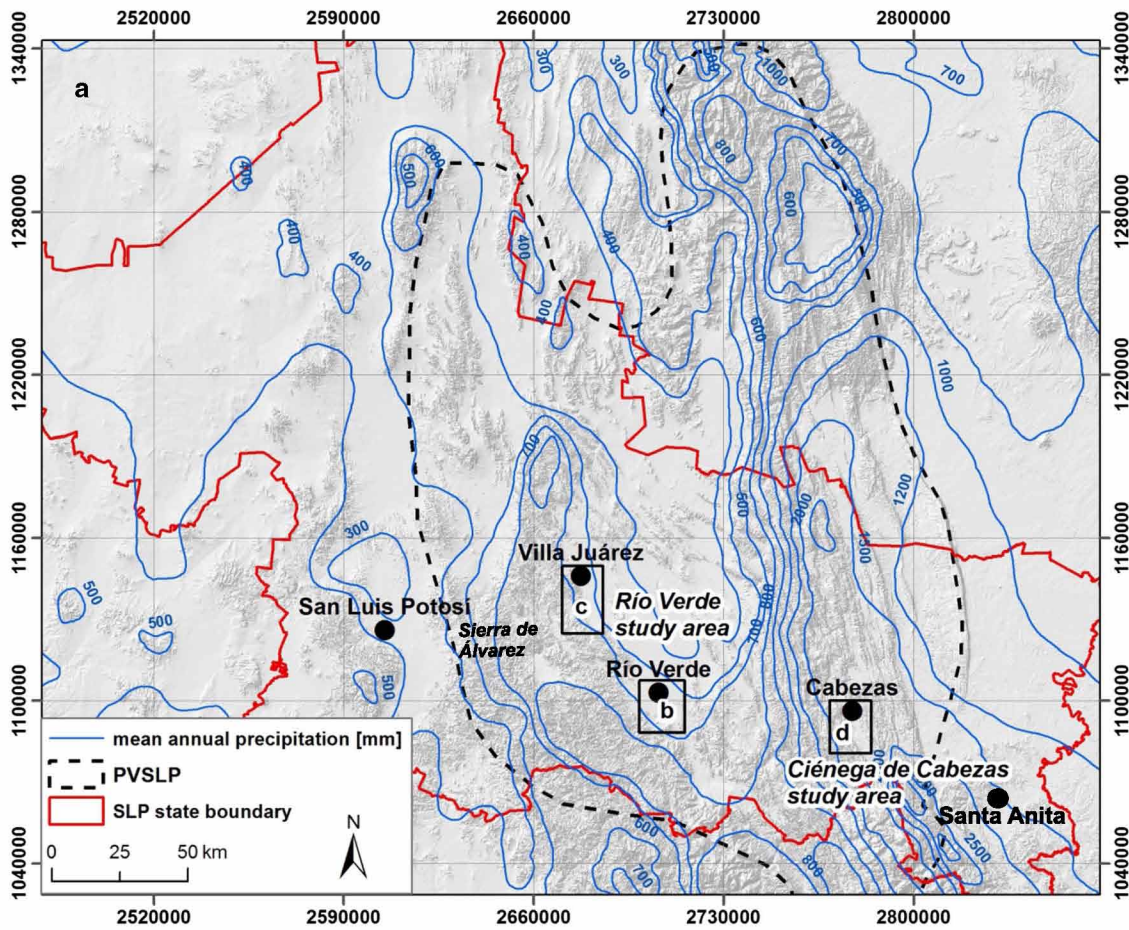


Fig. 2 a Geographical overview highlighting the location of the study areas within the state of San Luis Potosí (SLP) and the platform Valles-San Luis Potosí (PVSLP) with the mean annual precipitation (INEGI 2015); b–d Location maps with simplified lithostratigraphical units (modified after SGM 1997a, b, 1998) of the study areas in the Río Verde region including the subareas Media Luna channel (b) and Río Choy (c) with the sampling points R1–R31. Ciénega de Cabezas region (d) including the sampling points C32–C51. Note: Fm—Formation

added. All bottles were stored in coolers until analysis in the laboratory for water and soil of the Engineering Faculty of the Universidad Autónoma de San Luis Potosí (UASLP). The main cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Li^+ , and Sr^{2+}) were analysed by atomic absorption spectroscopy (AAS) and the anions (Cl^- , SO_4^{2-} , NO_3^- , and F^-) by spectrophotometry.

Accuracy was controlled by using laboratory duplicates of samples and by including standard solutions.

In order to evaluate the hydrochemical analysis, an ion-balance was applied: except for sample R10, sampled water from the stream “El Carrizal” with -32% , the errors stay within the $\pm 10\%$ interval and thus, only R10 is excluded from further interpretations. The error of sample R10 results of an uncompleted balance respective Fe^{2+} : based on the measured ion concentrations and physico-chemical parameters, it is probable that $\text{Fe}_2(\text{SO}_4)_3$ complexes are present in the water (Table 2). Nevertheless, results of sample R10 were considered in the discussion because the rest of the analysed parameters contribute to understand the studied flow system.

The sites at the location “El Carrizal” (R9, R10, R11) were visited again five years after the first field sampling.

Fig. 3 Groundwater contour maps of the year 2006 and 2007 of the RV study area (modified after CONAGUA 2015a, b); lithostratigraphical units (modified after INEGI 2017)

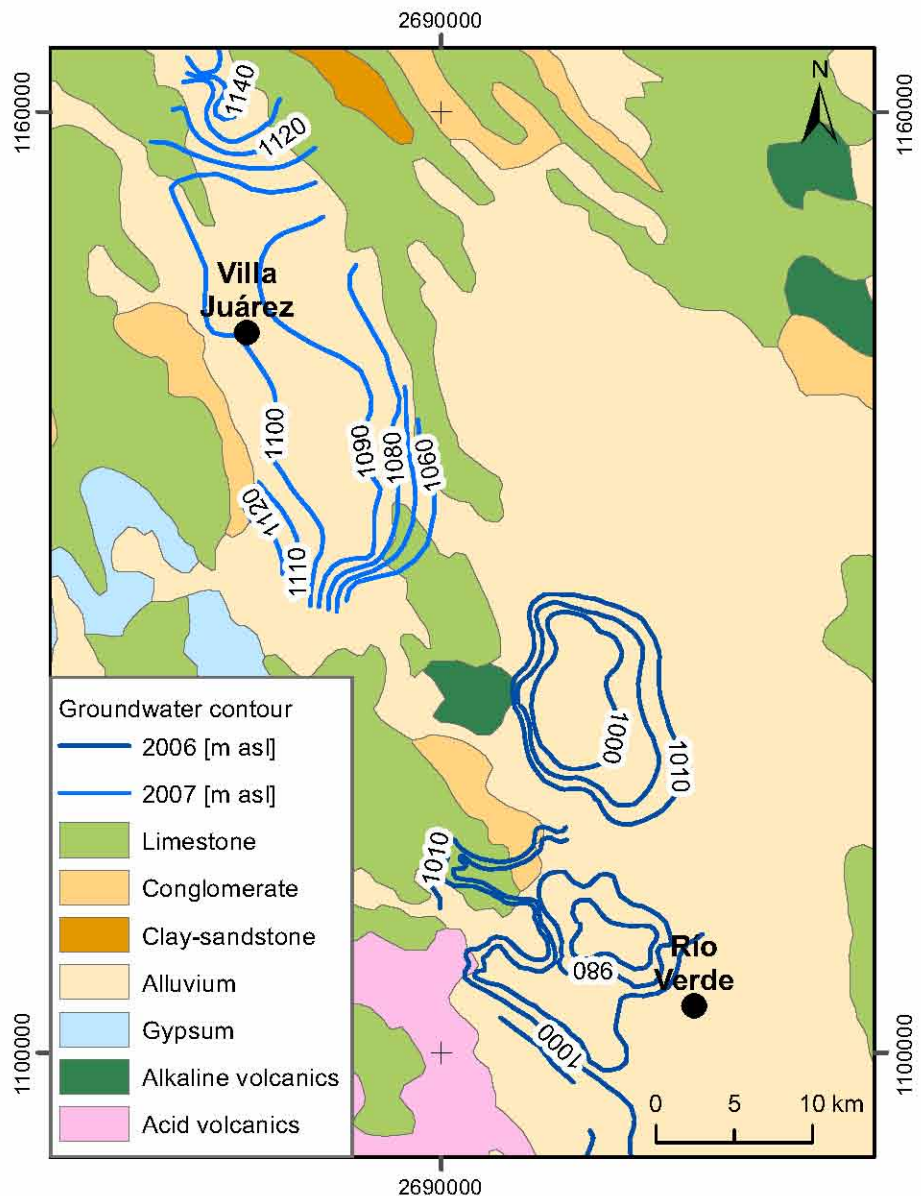
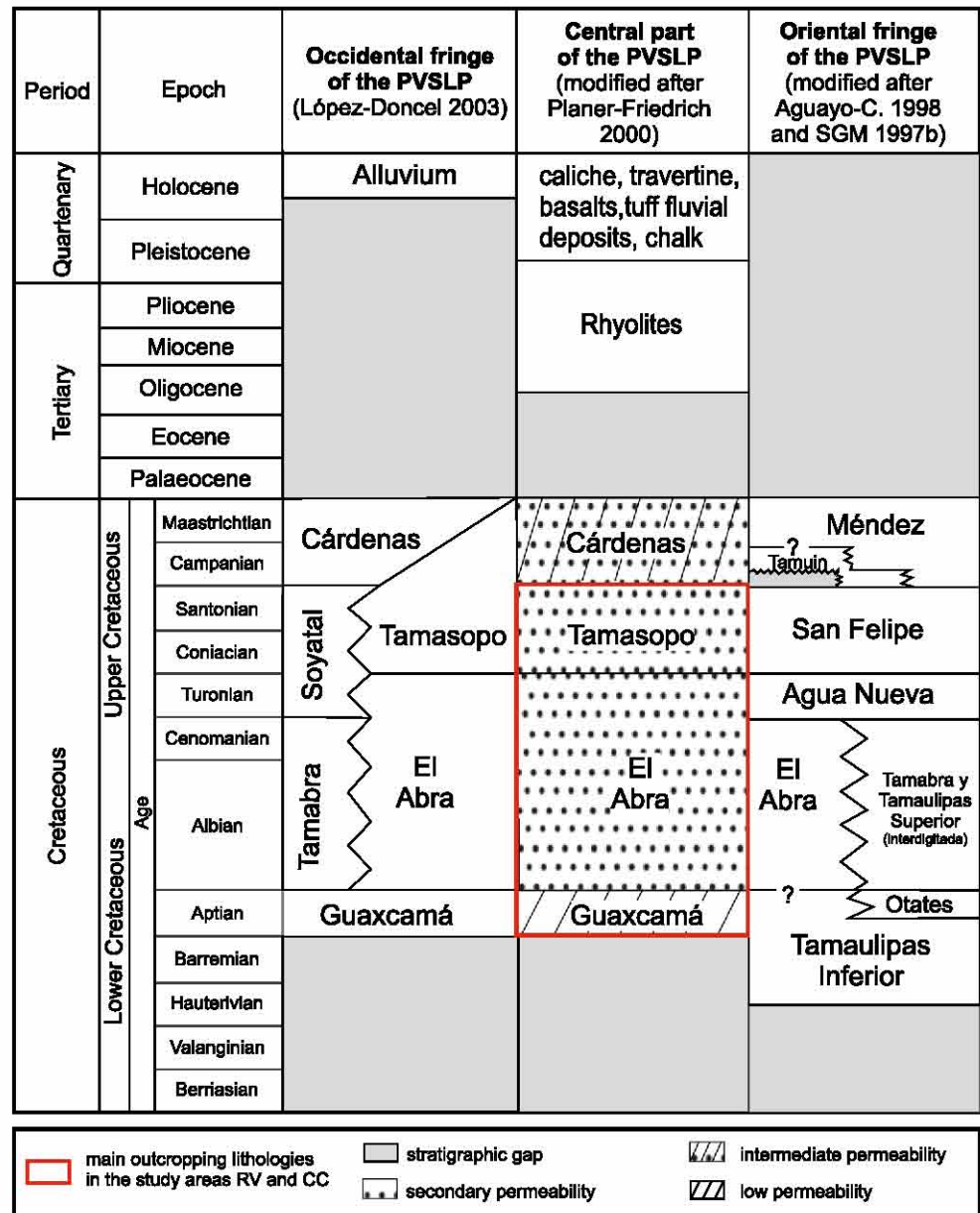


Fig. 4 Stratigraphic columns of the PVSLP, distinguished into the occidental, central and oriental fringe and signature of permeability characteristics of the main lithology in the study areas



Hydrochemical measurements and the chemical analysis were conducted in the same way as in the previous sampling campaign thus the results will be presented as comparative values and are not included in statistics and interpretations.

Saturation index of specific minerals and progressive modelling were calculated using the code *PhreeqC for Windows* with the databases *wateq4f.dat* and *PhreeqC.dat*, respectively.

To determine the discharge in laminar flow conditions, the flow velocity was measured with a flowmeter based on the travel time of acoustic waves reflected from particles in the water (ADC, OTT 2013). The measurement has to be repeated in different depth over a cross section of the stream in order to calculate the discharge over the integral.

This method was applied at 14 of the 51 selected sites. In turbulent flow conditions, the salt injection method as documented by Rantz (1982) was applied at 23 sites. Depending on the stream size and the estimated runoff, an amount in the range of 1–40 kg of NaCl was chosen. The salt was completely dissolved in a water-filled bowl and given as Dirac injections into the turbulent stream flow. Depending on the flow properties, the eC was measured some distance (about 20–40 m) downstream of the input location in intervals of 3 or 5 s, recording the peak of eC. The discharge was calculated after transformation of eC into concentration by an integration function of the peak area under consideration of the background conductivity of the stream water.