6 Preliminary Investigation of Groundwater and Surface Water Geochemistry in Campeche and Southern Quintana Roo

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6.1 Introduction1

This study of the hydrogeology of Campeche and southern Quintana Roo complements an earlier study of the northern part of the Yucatan peninsula. In the most north-western part of Campeche state, stratigraphy of aquifer rocks is continuous with that of adjacent Yucatan state, and groundwater geochemistry of chloride, sulphate, and strontium ions indicates that the major ion source for water wells of the city of Campeche is an underlying saline intrusion that is continuous with the intrusion in the western part of Yucatan state. Elsewhere in Campeche state and east of 90° 45' West (longitude of Escarcega), there is little or no geochemical evidence for a saline intrusion. In much of the southern part of the state, groundwater ion chemistry is dominated by dissolution of extensive beds of gypsum/anhydrite-bearing evaporite of probable Palaeogene age that releases sulphate and chloride ions to the aquifer. The evaporite also releases minor amounts of strontium, which is a useful tracer even at low concentration. This strontium apparently comes from the dissolution of the mineral celestite $(SrSO₄)$, which appears to be ubiquitous (although not abundant) in evaporite beds. Evaporites are also the major ion source for most of the groundwater of the southernmost part of Yucatan state and southern Quintana Roo. Groundwater in and near the valley of the Rio Hondo (along the Mexico-Belize border) has high concentrations of sulphate and strontium but unusually low concentrations of chloride. The ratio of sulphate to chloride and the ratio of $(Sr)/(Ca)$ versus 1/(Sr) are used here to evaluate ion sources of all samples in this study. Persistent clay is present in the lower Palaeogene rocks of southern Campeche. The clay units are highly impermeable, and they are capable of effectively isolating surface water from the sulphate-rich groundwater of the aquifer. The result is the formation of a large number of ponds, pools, and abandoned water-filled stream valleys, at least some of which contain water of exceptionally low ion concentration (in marked contrast to the sulphate-rich water of adjacent wells). This surface water may be a suitable source of potable water for communities in the area.

This study contributes to the understanding of water-rock interaction in the southern Yucatan peninsula. Identification of ion sources for the aquifer system is an important tool for water management in Campeche and Quintana Roo. Here we extend recently published research on the groundwater geochemistry of the northern Yucatan peninsula (Perry et al., 2009) into Campeche and southern Quintana Roo. Relevant details about regional hydrostratigraphy and methods of data acquisition and interpretation can be found in that paper and are only briefly summarized here. In particular, table 3 of Perry et al. (2009) describes the importance to hydrogeology of regional geological features including 'layer cake' carbonate stratigraphy, lack of surface drainage, importance of fault and fracture systems in channeling groundwater movement, contribution of the Chicxulub impact crater to stratigraphy and structure, importance and extent of a marine saline intrusion, and the value of evaporite beds and the spatially (and perhaps genetically) related impact of ejected layers as geochemical tracers.

Several geological formations present in Campeche are continuous with those of the north of the Yucatan peninsula; but folding is more common

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in the south; topographic relief is greater; some streams, wetlands, and lakes are present; and distinctive closed basins of various sizes, mapped as poljes, are important geomorphic features. The geology of south-eastern Campeche is complex and remains poorly studied (Schönian et al., 2005, 2008). A widespread geological unit, mapped as early Palaeogene (Servicio Geológico Mexicano, 2007), strongly influences groundwater geochemistry because it contains bedded evaporite consisting of gypsum and other relatively soluble minerals. Also, because of the high solubility of gypsum and other sulphate minerals, these beds, which may include impact ejecta and/or overlying evaporite beds of variable thickness, are poorly exposed. Their influence on hydrogeology is critical to this study, but knowledge of their full extent, thickness, and properties awaits detailed geological mapping.

6.2 Ions as Tracers in Yucatan Groundwater

There are two principal sources of ions in groundwater (and surface water) of the Yucatan peninsula; these are sea water from a major saline intrusion and dissolution of minerals from aquifer rocks. The inorganic ions that are most important in Yucatan groundwater geochemistry include HCO_3 , CO_3^{-2} , Cl, SO_4^{-2} , HS, Na⁺, K⁺, Ca⁺², Mg⁺², and Sr⁺². Sources and sinks for these ions are listed in Perry et al. (2002). Most of them are not useful in tracing natural ion sources on a regional scale because they (1) may have an anthropogenic source, (2) are present in similar abundance throughout the peninsula, or (3) are highly reactive and hence responsive to particular local environmental factors such as redox conditions and ion exchange reactions. Here we shall consider primarily abundance relations between the relatively conservative ions chloride, sulphate, and strontium as groundwater tracers. There is an additional advantage in using strontium as a tracer of ion sources. Its isotopic ratio (⁸⁷Sr/⁸⁶Sr) is often specific to a particular stratigraphic unit (Perry et al., 2009).

In northern Yucatan and Quintana Roo, sea water, modified by interaction with aquifer rock, penetrates far inland beneath a layer of less dense fresh water (Perry et al., 1989, 1995; Marin, 1990, 2007; Marin et al., 2000; Escolero, 2007; Escolero et al., 2000, 2002, 2005, 2007). Although the distance to which this intrusion penetrates has not been established, its presence near Santa Elena at UNAM5 [\(figure](#page-2-0) 6.1), more than 80 km from the coast of the Gulf of Mexico, has been documented (Perry et al., 2002).

Furthermore, there is a strong indication that sea water penetrates inland and establishes a counter-flow to fresh water movement through the permeable zone of the Ticul Fault at least as far inland as Tzucacab and Dziuche (Perry et al., 2009). The presence of this saline intrusion has important practical consequences. It establishes subsurface counter-currents and affects fresh water quality by mixing and/or upcoming in excessively pumped wells (Beddows et al., 2007; Escolero et al., 2002, 2007; Perry et al., 2002, 2009; Steinich/Marin, 1997; Stoessell et al., 1989).

Where a saline intrusion is present it contributes to the geochemistry of the overlying fresh groundwater by turbulent mixing. That contribution can be estimated from the chloride content and the ratio of the normally conservative ions, Cl and SO_4 (Perry et al., 1995, 2002; Escolero et al., 2005). The ratio of these two ions in sea water, expressed for convenience as $100[(SO_4)/(Cl)]$ (henceforth R) and measured in equivalents, is about 10.3. Groundwater beneath much of northern Yucatan and Quintana Roo has a relatively high concentration of chloride, and it has R values close to 10, suggesting that its chemistry is strongly influenced by interaction with the underlying saline intrusion (Perry et al., 2002).

R can be modified by chemical reaction, dissolution of aquifer minerals, or adsorption. Chloride is highly conservative – it has little tendency to interact chemically with the rocks of the aquifer. Although water will readily dissolve the highly soluble mineral halite (NaCl), that mineral is unlikely to persist in the permeable, well-washed rocks of the Yucatan aquifer except perhaps as inclusions in other less soluble minerals. Sulphate ion is less conservative than chloride. Its concentration in groundwater can increase if the aquifer contains gypsum $(CaSO_4 \cdot 2H_2O)$, anhydrite (CaSO4), or celestite, SrSO4. Conversely, sulphate concentration decreases if redox reactions in the aquifer convert sulphate ions to sulfide.

In previous research studies of Yucatan groundwater we have found it useful to compare strontium concentration to chloride and sulphate concentrations. Strontium, which can easily be analyzed at low concentrations, is the essential cation in celestite $(SrSO₄)$. It is also a minor ion in calcite, dolomite, and gypsum; and although aragonite can contain up to 7000 ppm, that mineral is uncommon except in the youngest carbonate rocks along the coastal fringe of the peninsula. Celestite is not abundant, but it appears to be ubiquitous in evaporite rocks of the peninsula.

Figure 6.1: Sites of sampling. **Source:** Research data on the geology and hydrogeology of the Yucatan peninsula. Location of sampling sites for this paper in Campeche and southern Quintana Roo are shown. Also shown are specific aspects of the hydrogeology of the northern peninsula. Unless indicated, these summarize information in Perry et al. (2009). Numbers in parentheses within sample bullets are R values for water samples from lakes and municipal wells $[R = 100[(Sr)/(Cl)]$ in meg/kg].

Groundwater that comes into physical contact with evaporite therefore may locally equilibrate with celestine, which can then control its strontium ion content. Perry et al. (2002, 2009) have presented evidence that the concentration of strontium in Yucatan groundwater is a reliable indicator of evaporite in the subsurface.

6.3 Chloride and Sulphate Ions in Groundwater of Campeche and Southern Quintana Roo

Our study of groundwater geochemistry of Campeche east of 90° 45' W (longitude of Escarcega, Campeche) indicates that a saline intrusion is limited to the northwest corner of the state and to a narrow coastal fringe. All of our samples from southernmost Quintana Roo have high R values and exceptionally low chloride concentrations. Together with strontium data presented below this indicates the lack of a saline intrusion over most of the area covered by this study (figure 6.1, [6.2](#page-3-0); [table](#page-4-0) 6.1). Four groundwater samples from north-west Campeche do show geochemical evidence of sea water influence.

RCARAC is from the shallow well on the property of a beachfront restaurant, less than 100 m from the Gulf of Mexico. The other samples from near the western (Gulf) coast that have R ratios of 12 to 16 (approximating that of sea water) are STAROSAP1, CHINAP and CHINAG [\(figure](#page-3-0) 6.2). On the basis of their strontium composition, each of these water sam**Figure 6.2:** Sulphate *vs*. chloride concentration. **Source:** Research data. Units on axes are in meq/kg. Diagonal line emanating from the origin is the sulphate/chloride ratio in sea water. Inset is a 'blow-up' of the origin. Samples within the smaller box are within US EPA recommended limits for drinking water. (Mexican recommended limit for sulphate in drinking water is 400 ppm (8.1 meq/kg)). Double arrow indicates surface water and well-water concentrations from the same town. Sites labelled 'West' are from near the city of Campeche and the Valle de Edzna. Those labelled 'Centre' lie along or near Mexican Highway 186. Those labelled 'East' are from near the Rio Hondo (Mexico-Belize border).

 \triangle Center o North East

ples probably also contains water from a third recharge source as is discussed in the section on strontium ion chemistry. STAROSAP1, CHINAP and CHI-NAG, which are water supply wells for the city of Campeche, all meet the Mexican drinking water norm for sulphate.

Rio Champoton, which enters the Gulf at the town of Champoton, drains the polje Valle de Edzna ([figure](#page-2-0) 6.1). It is represented by sample ZAPB, which has a high strontium content and an R value of 72 and thus, except for a relatively high chloride content of 7.3 meq/kg, shows no indication of interaction with sea water even though the sample was taken within about 15 km of the Gulf coast.

Water from well BSDG in Escarcega, the fourth most populous city in Campeche, has an R value of 31.6 and exceptionally low concentrations of chloride and sulphate (figure 6.2). The R value, which is only about three times that of sea water, could indicate a sea water component; however, on the basis of its low chloride and its strontium ion chemistry we consider it to have a different mixing history, as discussed

Table 6.1: Chemical data and probable ion sources for groundwater and surface water of Campeche and Southern Quintana Roo. **Source:** Data from research.

Notes: Sources: S = Saline intrusion; E = Evaporite; D = Dilution by water normal karst groundwater. Criteria: R = $[100(SO₄)/Cl]$; Sr = Position on [figure 6.3](#page-6-0).

below. UXMING, with an R value of 38, may have a sea water component. Its composition is also discussed further below with respect to its strontium chemistry.

A traverse westward from Escarcega to Chetumal along Mexican Highway 186 encounters groundwater with sulphate concentrations deemed too high for acceptable drinking water ([figure](#page-3-0) 6.2). This is the result of dissolution of sulphate from beds of Palaeocene gypsum [\(figure](#page-8-0) 6.4) such as those exposed to surface weathering east of Concepcion, Campeche state (labeled CONCE in [figure](#page-2-0) 6.1).

Because all the water encountered in wells drilled in eastern Campeche has an exceptionally high sulphate concentration, CONAGUA has installed an aqueduct to deliver water to Xpujil from wells near Concepcion. Representative municipal well samples from the area include ZOHLP and '20 NOV', which have almost four times the Mexican recommended maximum value of 400 ppm (8.3 meq/kg) for drinking water [\(figure](#page-3-0) 6.2). One of three samples from the vicinity of La Guadalupe (LAGUAD on [figure](#page-2-0) 6.1) contains more than 36 meq/kg (1750 ppm) of sulphate.

6.4 Groundwater from Northwestern Quintana Roo

In order to present a complete survey of groundwater geochemistry of the Yucatan peninsula we present here analyses of a suite of samples from the Holbox Fracture Zone in the farthest north-eastern part of Quintana Roo [\(figure](#page-2-0) 6.1; Tulaczyk et al., 1993). These data are instructive because they illustrate the characteristics of dilute groundwater in a region of high recharge in which the water chemistry is dominated by a saline intrusion. All of these samples have R values between 7 and 26, with an average of 16. Although this value is high compared to the sea water ratio of 10.3, these waters are very dilute and hence readily subject to contamination by surface processes. The largest spring, Yalahau [\(figure](#page-2-0) 6.1) has an R value of 10.6 and may be sampling a representative part of the aquifer. We tentatively conclude that, in contrast to the waters of Campeche, these waters have a simple history and derive most of their ion content from sea water.

6.4.1 Strontium Ion as a Groundwater Tracer

A useful groundwater and surface water geochemical diagram is one in which the ratio 1000 $[(Sr)/(Cl)]$ is plotted on a logarithmic scale vs*.* the reciprocal of strontium concentration. In a diagram of this kind, binary mixtures of two waters differing in their strontium and chloride concentrations plot along straight lines.² [Figure](#page-6-0) 6.3 is a strontium/chloride plot of data of this study (listed in [table](#page-4-0) 6.1). For comparison, figure [6.3](#page-6-0) also includes data from the adjoining region, Yucatan state and northern Quintana Roo, which were published by Perry et al. (2009). Comparison of the two data sets is especially helpful because, whereas we do not yet have strontium isotope data for the samples in [table](#page-4-0) 6.1, strontium isotope analyses were available to help identify mixing trends in the earlier data set from Quintana Roo and Yucatan State (Perry et al., 2009).

The inset in [figure](#page-6-0) 6.3 shows various mixing trends for a water, X_1 , in chemical equilibrium with an evaporite that contains gypsum, celestite, and some trapped inclusions of highly soluble halite (NaCl), the latter acting as a source of chloride ions. Because of its high strontium concentration, water X_1 will occupy the left-hand side of the diagram. Mixtures of X_1 with waters A or B will appear as straight lines (X_1A, X_1B) . Mixtures along path X_1C are more difficult to explain because they would imply existence of a water of composition C, which was otherwise dilute but that had a high content of strontium. One way of moving along path C would be to have a dilute water that flowed continuously over an evaporite, washing away its most soluble phases such as halite. Alternatively, the evaporite unit corresponding to C may have a different composition (higher in NaCl) than the unit at $X₁$. This is not a hypothetical question; it involves how to best interpret actual samples from south-western Quintana Roo that appear in the upper left corner of [figure](#page-6-0) 6.3.

Note that the composition of water X depends on the origin of the water that maintains contact with the evaporite. For example, if evaporite is present in the part of the aquifer within the chloride-rich saline intrusion, the resulting water will occupy a position on the diagram similar to X_2 . This is the case of water from Xkolac and other deep cenotes shown in figure 6.2 of Perry et al. (2009). For further discussion of the behaviour of water in deep cenotes, readers are referred to that paper.

6.4.2 Evaluating Inorganic Ions

From [figure](#page-6-0) 6.3 it is apparent that STAUROSAP1 and RCARAC are very similar to the coastal waters Celestun WW, Estero Pozo, and El Remate (Perry et al.,

² Note that in this plot of $I/(Sr)$ the samples with the highest strontium concentration plot nearest the origin.

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Figure 6.3: Sulphate *vs*. chloride concentration. **Source:** Research data. Vertical axis is 1000[(Sr)/(Cl)]. Horizontal axis is 1/(Sr). Both axes are in units of millimoles/kg. On this plot, mixtures of two waters plot along a straight line. Labels as in [figure 6.2](#page-3-0). In addition, diamonds are samples from Yucatan state and northern Quintana Roo (taken from Perry et al., 2009).

2009). The hydrogeology of those waters from the earlier study is instructive. Each is a coastal well near the terminus of the major underground flow system running along the Ticul Fault and the western arm of the Ring of Cenotes (Perry et al., 2009) that is marked in [figure](#page-2-0) 6.1. That shows the progressive change in sulphate/chloride ratios as that evaporite-laden water moves north-west from Lake Chichancanab toward the Celestun estuary. The straight mixing line between water samples from L. Chichancanab and Celestun WW in figure 6.3 passes through water samples from the municipal water supplies in Peto and Tzucacab. These are all waypoints for water originating in the vicinity of the lake and moving through the Ticul Fault system and the Ring of Cenotes. As it flows northwestward, this water mixes with other groundwater and with the underlying saline intrusion. By analogy with the waters from Yucatan state, STAUROSAP1 and RCARAC can be seen from figure 6.3 to be threeway mixtures of sea water, dilute groundwater, and water draining an evaporite terrain. Also, UXMING lies along a mixing path (like path A in the schematic

of [figure](#page-6-0) 6.3) that is identical to the mixing line connecting water from Celestun WW and Peto in Yucatan.

Samples HOOL, BSDG (supply well for Escarcega), SIPH2, EDZNA, TIXM, and CAMP lie on or near a mixing line shown as a dashed line in figure 6.3, which connects dilute lagoon water ZOHLL and highly concentrated evaporitic water from the adjacent well ZOHLP. This path is analogous to path B in the schematic of [figure](#page-6-0) 6.3.

Compared to groundwater from the north-eastern and north-central peninsula, water from that part of southern Quintana Roo along the escarpment of the Rio Hondo that borders Mexico and Belize has high strontium and sulphate and exceptionally low chloride concentrations ([figures](#page-3-0) 6.2, [6.3](#page-6-0)). Samples of this suite are from 1) springs debouching metres to tens of metres above the Rio Hondo valley floor, 2) municipal wells, and 3) the Rio Hondo itself. In addition, one sample is from Lake Bacalar. These samples are all similar in composition to water from Cenote Azul, sampled previously (Perry et al., 2009). They appear to be effectively isolated from sea water and hence indicate the absence of a saline intrusion. That observation is strengthened because Cenote Azul, which is near the coast ([figure](#page-2-0) 6.1) is at least 65 metres deep, yet its water is constant in composition and exceptionally low in chloride over the entire depth range. These samples follow path X_1C in the schematic diagram in [figure](#page-6-0) 6.3. The precise reason that water in close contact with evaporite should vary is not possible to determine from data available at this time. It is important to note that whatever the exact mechanism, these samples have not exchanged with sea water or with a saline intrusion.

Bacalar Pozo 2, a water supply well for the town of Bacalar, is several km north-west of the town (figure [6.1](#page-2-0)). It does not evidence the same degree of strontium enrichment/chloride depletion shown by other samples of the eastern sample suite.

Several samples in south-central Campeche come from wells that are exceptionally high in sulphate. LAGUAD and LAGUADL are from shallow dug wells within the town of La Guadalupe. They are severely contaminated as indicated by nitrate concentrations of 4 and 8 meq/kg respectively. A nearby spring (LAGUAD) flows out from an outcrop of gypsum. ZOHLP and '20 NOV' are nearby municipal pumping wells. Gypsum and anhydrite outcrops are common in this area ([figure](#page-8-0) 6.4), and sulphate in water here is sufficiently objectionable for drinking that CONAGUA has installed an aqueduct to provide potable water to part of the area.

Note that water from these wells contains significantly more chloride than water from the Rio Hondo region. It seems likely that the evaporite here contains an appreciable amount of halite as inclusions protected from dissolution until it is released when surrounding crystals of gypsum dissolve.

6.5 Perched Water Table

Extensive layers of clay are present in southern Campeche and southern Quintana Roo, and these act effectively as aquitards, trapping meteoric precipitation in ponds and lakes throughout the region. The largest of these is Lake Silvituk (SILV: [figure](#page-2-0) 6.1; table [6.1](#page-4-0)) with chloride and sulphate concentrations respectively of 0.2 and 0.04 meq/kg, yielding a near-sea water R value of $9.8³$. Water from another small lake illustrates the sealing value of the local clay aquitard. Sample ZOHLL is from a lake on the edge of the small town of ZOH. Its water has among the lowest concentrations of sulphate [\(figure](#page-3-0) 6.2), yet water from the municipal well, ZOHLP, has one of the highest sulphate values encountered in this study.⁴

6.6 Suggestion for Further Investigation

Adequate drinking water of desirable quality is difficult to obtain in eastern Campeche. Drilling has not encountered water of low sulphate content. However, this area has a unique system of internal streams and ponds supported by one or more layers of highly impermeable clay (one or more of which may have developed from lapilli of K/Pg impact ejecta (Schönian et al., 2005, 2008)). [Figure](#page-9-0) 6.5 shows one example of a lake that once was a meandering stream. Our results show that this surface water can be of very good quality [\(figure](#page-3-0) 6.2). In a region with 1,200 mm of annual rainfall, it may be useful to evaluate the possibility of developing this surface water as a resource in this region with a growing population.

³ It is much more likely that this R value is the result of atmospheric transport or even coincidence than that it is produced by contact with a saline intrusion.

⁴ Even the nitrate content of the three surface water bodies sampled was below the limit of detection, presumably because available nutrients were consumed by plant growth.

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Figure 6.4: Bedded gypsum outcrop about 20 m high on highway 186 east of Concepcion, Ouintana, Roo (CONCE in figure 6.1). **Source:** Photo from research of the authors.

This pond occupies a meandering channel apparently vacated by a stream as a result of drop in the water table. Closed internal basins drained from below (mapped as poljes) are common in this area. Whereas groundwater has uniformly high sulphate content, lakes and ponds from here tend to have water with low salinity.

6.7 Summary and Conclusions

This study has determined the major ion sources for a large and developing region whose complex geology and hydrology have received little study. The ion sources for a representative suite of water samples analysed for this study have been discussed in detail. In [table](#page-4-0) 6.1, we have specified the probable major ion sources for all water in the study, and we have listed there the criteria that led us to those conclusions.

A saline intrusion extends south from Yucatan state into the north-west corner of the state of

Figure 6.5: A pond in southern Campeche (located in figure 6.1). **Source:** Photo taken during the authors' research.

Campeche. Near the city of Campeche the fresh water aquifer is likely to be underlain by a saline intrusion. This intrusion does not extend far south of the city of Campeche. [Figure](#page-3-0) 6.2 shows that potable water is present in and around the Valley of Edzna, but east of Concepcion, Campeche; groundwater is heavily contaminated by sulphate ion contributed by extensive evaporite deposits. Dissolution of evaporite also dominates groundwater geochemistry along the Rio Hondo in southern Quintana Roo.

It is unlikely that groundwater of good quality will be found in eastern Campeche. However, the occurrence of abundant beds of impermeable clay in that region suggests that it may be possible to exploit natural surface water sources and to develop new surface sources of good quality there.

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