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Mixing Corrosion in a Coastal Aquifer

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MIXING CORROSION IN A COASTAL AQUIFER

By

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ABSTRACT

The coastal aquifer of the northeastern Yucatan peninsula is a mixing zone where freshwater from the platform interior mixes with seawater and saline groundwater to form new brackish solutions. The brackish solutions may form stable flows that move seaward through the aquifer as discrete water parcels. These flows frequently have lowered pH, may be undersaturated with respect to calcite, and may produce significant regional-scale porosity changes due to mixing corrosion.
CHAPTER 1
INTRODUCTION

As physico-chemically heterogeneous waters mix there is a complex interaction of chemical and physical processes. These chemical and physical processes may produce wide-ranging and geologically significant effects (Bogli, 1964; Thraillkill, 1968; Runnels, 1969; Plummer, 1975; Wigley and Plummer, 1976). Over the past three years, I studied modern mixing processes in a coastal carbonate aquifer in the northeastern Yucatan Peninsula, Mexico. I refer to this study area as the Tulum Research Area or TRA. The intent of this study was to assess the potential for carbonate dissolution due to mixing effects in a real-world environment. This thesis summarizes the findings of my study.

Introduction to Mixing Zones

In the environment, areas where heterogeneous waters mix may simply be called "mixing zones" (Backet et al., 1986; Smart et al., 1988; Stoesse et al., 1989), but what exactly is a mixing zone? What defines a mixing zone and at what scale does it operate?

For the purposes of this work I define a mixing zone as a region where two heterogeneous solutions actively mix to produce detectable volumes of a measurably different solution. This definition is obviously scale dependent. Mixing zones vary widely in scale from sub-millimeter sized zones in porous media to regional-scale aquifers that may be hundreds of
square kilometers in size. In this work I am primarily concerned with regional-scale mixing, although I will address mixing on a smaller scale as it relates to regional-scale processes.

**Coastal Mixing Zones: Estuaries and Aquifers**

A coastal mixing zone is a region where terrestrial fresh water mixes with seawater or saline groundwater (often geochemically evolved seawater). Coastal mixing zones may be divided into two broad categories: estuaries and coastal aquifers. Apart from the obvious difference in surface versus subsurface location, there is significant commonality between these two environments. The degree of similarity in these two environments led Moore (1999) to coin the phrase "subterranean estuary" to describe the zone where fresh groundwater and seawater mix in coastal sediments. The aquifer of the TRA can accurately be described as a "subterranean estuary" and some interesting and useful aspects of this relationship will be introduced throughout this text.

**Mixing Zone View**

A generalized coastal mixing zone aquifer can be crudely visualized in profile or plan view (Figure 1.1). Versions of this diagram are commonly reproduced in the literature, but the diagram is based more on preconceived ideas and less on actual data from real locations. In reality, any coastal mixing zone is a very complex three-dimensional form that is in dynamic equilibrium with numerous environmental factors. Figure 1.1 is oversimplified to such a degree that it is of little use other than to serve as a reference point for future clarification. The specific location and dynamics of the mixing zone in the TRA is covered in subsequent chapters.
Figure 1.1 Conceptual Coastal Mixing Zone in plan and profile view. Note that while various versions of this diagram are commonly promulgated, the diagram is very poorly defined.

Intent and Scope of this Work

Intent

In this work, my intent is to address the following: (i) coastal mixing zone morphology and function, (ii) important chemical and physical concepts that can be used in mixing zone studies, (iii) measurable parameters that quantify chemical mixing processes and effects, (iv) a sampling and analysis strategy (including both field and laboratory methods), and (v) important conclusions from my field research projects in the TRA.
Scope

Although my focus is exclusively on the coastal aquifer of the northeastern Yucatan Peninsula, I will attempt to define many chemical and physical concepts broadly so that they may be applied to other coastal aquifer study locations without great modification.

This study was primarily designed to examine the chemistry of the coastal mixing zone aquifer. However, there is an intractable link between chemical and physical processes in mixing zones and to completely ignore the physical processes would greatly denigrate any conclusions drawn about the chemical system. Unfortunately, given the scope of this thesis, I cannot include a detailed, quantitative treatment of the physical processes operating in mixing zones. As a compromise, I will only qualitatively describe physical concepts that are essential to the discussion of mixing zone chemistry. A much more detailed study of the physics of mixing is clearly warranted.

Problem

On my field research projects in the Yucatan, I found several zones with greatly enhanced bedrock porosity near active freshwater-saltwater mixing sites. Many researchers have previously reported this same porosity-mixing relationship (Back et al., 1986; Smart et al., 1988; and Stoessel et al., 1989). The possible geological implications of such mixing may include speleogenesis (Dreybrodt, 1981; Mylorie and Carew, 1990) and regional-scale porosity enhancement (Baceta, et al., 2001). Thus it is well established that enhanced porosity and mixing are often correlated, but can it be demonstrated that mixing is the cause of this enhancement?
Logical Caution

Even though there is often a strong correlation between the location of active mixing and bedrock with enhanced porosity, it is presumptuous to state that mixing effects have directly caused porosity enhancement until a detailed chemical analysis of all mixing solutions has been completed. It may be that active mixing is only correlated with enhanced porosity, but not the cause of its development. The investigation of this kind of mixing system must be carefully designed to avoid tautological errors in logic.

Hypotheses

I am primarily interested in the thermodynamic potential for calcite dissolution by the mixing of saturated waters (from this point forward, saturation state will always be with respect to calcite unless specified). I am seeking to produce a robust chemical model, based on actual real-world data, that will demonstrate that carbonate dissolution by mixing effects is thermodynamically possible. This model will be based on the theoretical work of Bogli (1964) and Plummer (1975) and will incorporate new field data that I collected in Mexico. This work is intended to verify existing geochemical theory (Bogli, 1964; Plummer, 1975), to elucidate physical hydrologic processes in the mixing zone, and then to link the geochemical and hydrologic processes together in a rudimentary model. I have separated my hypotheses into two categories: (i) a core hypothesis and (ii) secondary hypotheses phrased as questions.
**Core Hypothesis**

I have designated the hypothesis below as my core hypothesis. If this core hypothesis is supported then a number of other questions immediately arise and are addressed below as secondary questions.

Core Hypothesis: The mixing of saturated freshwater and saltwater in a coastal mixing zone can produce a solution that is significantly undersaturated with respect to calcite.

If mixing produces an undersaturated solution, then dissolution of carbonate minerals is only possible, but not proven or demonstrated. By focusing solely on the chemistry of the mixing solutions, and not on rock composition or physical constraints, only the potential for dissolution of carbonate rock is tested. To ask if these solutions actually dissolve carbonate rock in a real-world environment, with all constraints and variables, is a different question entirely.

**Secondary Questions**

These secondary questions primarily seek to clarify details and assess the significance of the core hypothesis. They are phrased as questions, not formal hypotheses, because my study design will not address them in sufficient detail to be entirely conclusive.

Secondary Question A: In the TRA, is the quantity of undersaturated water produced through mixing large enough to cause carbonate dissolution on a geologically significant scale?
Although the production of any volume of newly aggressive solution by mixing is interesting, I am concerned with the potential for regional-scale, geologically significant effects. Two criteria must be met to produce geologically significant dissolution: (i) a newly mixed solution must be undersaturated with respect to calcite, and (ii) a significantly large flux of this undersaturated solution must contact soluble carbonate rock.

Secondary Question B: Is the modern mixing zone representative of mixing zone chemistry over geologically significant periods of time?

If a modern mixing zone is to be used as analog for paleo-mixing zones, some consideration must be given to ensure that the modern mixing zone is actually representative of these past environments. Have the mixing zone processes and morphology changed substantially over time? Environmental factors that may have changed over time must be taken into consideration (i.e. sea-level change, seawater pH, etc.). What is the time scale required for mixing processes to produce geologically significant dissolution effects? Given the number of variables involved, this "geologically significant" period of time is very difficult to estimate accurately. As a crude, initial estimate I will assume that one million years would be sufficient time for mixing processes to cause significant geological change.

Secondary Question C: What specific chemical effects produce the undersaturation?
Complex combinations of chemical effects occur simultaneously in mixing zones. If mixing produces undersaturation, which specific chemical effects are primarily responsible, and which are less significant? The separation of these effects is difficult but necessary if the findings of this study are to be applied more universally.
CHAPTER 2

PROCEDURE

To test my primary hypothesis, I designed an investigative procedure with the following objectives:

1. Delineate the coastal mixing zone in the TRA and identify individual mixing sites within the overall mixing zone.
2. Create a series of water column profiles to map stratified flows and to collect in situ geochemical data at each water sampling site.
3. Collect a series of water samples suitable for geochemical mixing simulations.
4. Analyze the water samples for important geochemical parameters.
5. Use geochemical data from water samples, in conjunction with the aqueous geochemical modeling program PHREEQC-2, to determine if unsaturated solutions can be produced by mixing saturated end members.

The procedure can be separated into three sections: (i) field investigations and sampling, (ii) laboratory analysis, and (iii) aqueous geochemical modeling.
Field Investigations and Sampling

My fieldwork had two major components: water sampling and water column profiling. The two are closely related. The aquifer in the TRA is strongly stratified, so samples must be very precisely collected. A sound understanding of “hydrostratigraphic context” is necessary for meaningful sample collection. For example, two samples collected less than one meter apart in depth could vary in salinity by more than 34 PSU. By mapping stratified flows by profiling, I could identify very specific sampling locations that would be useful in later aqueous geochemical modeling efforts. The profiling also enabled me to put the samples into context.

Water Column Profiling

Mapping of the mixing zone with the MiniSonde 4 formed the foundation of my field investigation. This mapping fulfilled two goals: (i) to record \textit{in situ} values of certain parameters needed for aqueous geochemical modeling, and (ii) to acquire data that could be used to map the extent of the modern mixing zone and morphology of individual density strata.

Profiling Method

I used a Hydrolab MiniSonde 4 is a multi-parameter probe to create water column profiles. The Hydrolab MiniSonde 4 is capable of measuring and logging the following: pH, specific conductance (SpC, in mS/ cm), dissolved oxygen (DO, in mg/ L), temperature (T, in Celsius), oxidation-reduction potential (ORP, in mV), and depth. The MiniSonde 4 can be programmed to record a suite of data (all parameters) at a set time interval. I selected the minimum time interval (five seconds) allowable by the instrument’s software.

To create a water column profile, I lowered the instrument slowly through the water column as it logged data. The lowering rate varied depending on conditions. For example, in the open ocean profiles were created at a lowering rate of approximately one meter per second while
in the more intricately stratified inland cenotes the lowering rate was sometimes as low as one meter per minute. By lowering the instrument very slowly through the water column, the instrument’s various electrodes had time to ‘equilibrate’ with the ambient solution composition. Through experimentation in the field I found that the MiniSonde responded to changes in solution conductivity and temperature very quickly (<1 second). pH was slower to reach stable values when the probe was introduced into a new solution (~5 seconds). Dissolved oxygen was the slowest parameter to reach stable equilibrium (5 to 15 seconds depending on conditions).

The water column profiles created using the Hydrolab MiniSonde 4 multi-parameter probe are displayed in Appendix B. Selected annotated columns are shown in Appendix A. The MiniSonde automatically calculates salinity from the specific conductance measurement. The specifications of this instrument are shown in Appendix H.

**Water Sampling Plan**

Water sampling sites were selected to provide: (i) a range of representative end-member solutions to be used in speculative geochemical calculations, and (ii) actual mixing end-members, and the resulting mixed solution, from a selected mixing site within the TRA. The actual sampling sites are covered in greater detail in Chapter 3. A list of the water samples collected for this study and a description of each sample’s position in the water column is reported in Appendix C.

**Water Sampling Methodology**

My sampling program had two components: (i) collection of water samples for later laboratory analysis and (ii) onsite measurement of various parameters using a submersible multi-parameter probe (Hydrolab MiniSonde 4).
Sample Collection. Water samples were collected in one-liter polycarbonate bottles. Two bottles were filled at each sampling location. One sample bottle was used onsite for measurements of pH, conductivity, and temperature. The duplicate sample was transferred to an acid-washed, high-density polyethylene (HDPE) bottle for storage until later lab analysis. These samples were stored in the dark and cooled to approximately 2°C.

Onsite Parameter Measurements. Parameters needed for PHREEQC-2 modeling include pH, temperature, and conductivity. I used the MiniSonde 4 to record in situ values for these parameters at each sampling location.

Laboratory Analysis

The water samples were split into two sub-samples for anion and cation analysis by different methods.

Anions. Anions (Cl⁻, SO₄²⁻) were determined by ion chromatography. These results are reported in Appendix E.

Cations. Cation analysis (Ca²⁺, Mg²⁺, Na⁺, K⁺, Sr²⁺) was attempted with inductively-coupled plasma mass spectroscopy (ICP-MS). This procedure was problematic and did not yield useful results. Partial results are reported in Appendix D. Details of analytical problems are covered in Chapter 8. Given the unacceptable results from the ICP-MS analysis, I sent a sub-set of samples to a commercial lab to be run by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The ICP-AES analysis also did not return acceptable results.
Aqueous Geochemical Modeling

PHREEQC-2

PHREEQC-2 is a hydrogeochemical modeling program capable of calculating saturation indices for solution mixtures (Parkhurst and Appelo, 1999). PHREEQC-2 is the updated version of PHREEQE, a geochemical reaction modeling program that is has been used in previous mixing zone studies (Back, et. al., 1986; Sanford and Konikow, 1989; Price and Herman, 1991; Wicks and Herman, 1996).

I intended to use PHREEQC-2 to generate saturation indices for various speculative mixtures of sets of water samples. The data for this modeling would have come from the cation and anion analysis and the in situ geochemical data collected with the MiniSonde.
CHAPTER 3
STUDY AREA

Introduction

The primary study area for this work was a ~100 km$^2$ area in the state of Quintana Roo, Mexico (Figure 3.1). My study was based out of the small town of Tulum and I refer to the study area as the Tulum Research Area (hereafter TRA). Most of my fieldwork took place in this area, but in addition to the detailed work in the TRA, I also visited a number of other sites throughout the states of Quintana Roo and Yucatan. These other sites are located throughout the peninsula interior, along Rio Lagartos, and near Laguna Bacalar (Figure 3.2). I visited these sites to assess regional heterogeneity in geomorphology and hydrology. I found that TRA is a unique area that is not necessarily representative of the karst hydrogeology of other regions of the Yucatan.
Figure 3.1. The Tulum Research Area or TRA.

Figure 3.2. Yucatan Study Area and Tulum Research Area (TRA).
Site Locations in the TRA

In the TRA, *cenotes*, or sinkholes, are densely concentrated in the ~ 10km wide coastal mixing zone. In order to define the boundaries of the mixing zone, I wanted to sample at sites across the coastal mixing zone in transects aligned roughly perpendicular to the coastline. I completed two transects that I refer to as the North Transect and the South Transect. The names of the individual sample locations that make up each transect are given in Table 3.1 and displayed in map view in Figure 3.3.

Table 3.1. Cenote sample sites along two transects.

<table>
<thead>
<tr>
<th>North Transect</th>
<th>South Transect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cenote Conquistador</td>
<td>Sistema Naharon</td>
</tr>
<tr>
<td>Cenote Carwash</td>
<td>Maya Blue</td>
</tr>
<tr>
<td>Tortuga</td>
<td>Ox Bel Ha (Cenote Del Mar)</td>
</tr>
<tr>
<td>Grand Cenote</td>
<td></td>
</tr>
<tr>
<td>Sac Aktun</td>
<td></td>
</tr>
<tr>
<td>Temple of Doom</td>
<td></td>
</tr>
<tr>
<td>Cenote Abejas</td>
<td></td>
</tr>
</tbody>
</table>
Regional Karst Environment

Karst Geomorphology

Sinkholes that intersect the water table are common across the Yucatan and are known locally as cenotes. These cenotes are often collapse features that intersect underwater conduits at depth. Elevations in the TRA are commonly below 3 meters and rarely exceed 10 meters above sea level. Given the low topographic relief in the TRA, extensive dry caves are relatively uncommon within the 5km-wide coastal zone. However, very extensive conduit systems are commonly present below the present-day water table.

Karst Hydrology

The hydraulic gradient in the northern and northeastern Yucatan, as revealed by water level in cenotes, is easily observed to be quite low. However, the hydraulic gradient is very poorly quantified with only a few surveyed positions across the peninsula. Back and Hanshaw
(1970) estimated the gradient to be 1.4m over 80km using a single site at Chichen Itza as a
datum. Moore et. al., (1992) reported hydraulic head of 40cm to 60cm above mean sea level
between 2km and 4km from the coast.

In the TRA, and across the northeastern Yucatan peninsula in general, nearly all drainage
of upland areas is underground through karst conduits. The few surface streams exist only along
coastal marshes and estuaries. Unlike the state of Florida where rivers (e.g. Suwannee River and
St. Johns River) extend for significant distances inland and provide outlets for groundwater
discharge, the Yucatan study area has no similar outlets.

All groundwater from the Yucatan peninsula interior must travel for extensive distances
before reaching the coast. This long residence time may contribute to the saturated or
supersaturated state of the freshwater lens as it nears the ~ 10km wide coastal mixing zone.
Evidence of this saturation state is given by extensive formation of calcite rafts (thin wafer-like
flakes) where groundwater is exposed to the atmosphere and off-gassing of carbon dioxide can
occur.
CHAPTER 4
THE TULUM RESEARCH AREA COASTAL MIXING ZONE:
PRESENT AND PAST

Introduction

In the first chapter, I gave a very general definition of what a mixing zone is. In this chapter I explain the Tulum Research Area (TRA) coastal mixing zone in greater detail.

Mixing Zone: Present

Observation of Coastal Mixing Zone

In the Yucatan peninsula interior, the salinity of uppermost groundwater lens exposed in cenotes is consistently below 1PSU (see Appendix G for salinity notes). However, within the ~10km-wide zone along the coast, this lens becomes increasingly saline with proximity to the coast. The gradual increase in salinity is evidence of extensive mixing across density interfaces at depth (see Chapter 6). By examining the change in salinity of the uppermost ‘freshwater’ unit, it is possible to approximate the extent that this freshwater lens has mixed with the underlying saline groundwater (see Appendix L). This zone of active and extensive mixing, as revealed by contrasts in groundwater salinity, defines the Coastal Mixing Zone in the TRA.
Coastal Mixing Zone Morphology

Mapping the Mixing Zone

I mapped the extent of the modern TRA mixing zone by creating a series of water column profiles in a transect leading inland from the coast. Two critical pieces of information are present in the water column profile data: (i) the depth of the freshwater-saline groundwater interface (primary halocline), (ii) the salinity of the uppermost groundwater strata (top of freshwater lens).

Defining the Mixing Zone

The exact boundaries of a coastal aquifer mixing zone are difficult to delineate precisely with the paucity of sites (wells, cenotes, etc.) that are commonly available for data collection. Given the variability in mixing zone morphology with long-term (e.g. sea-level change) and short-term (e.g. a tropical storm) processes and events, there are no absolute and permanent boundaries. However, it is useful to be able to set some general boundaries for the system so that it can be discussed with clarity.

Setting Boundaries

There are several critical points in a mixing zone cross-section that can be defined by salinity contrasts. These boundaries include: the inland edge, the bottom, the top, and the oceanic discharge limit (Figure 4.1).
Inland Edge. The inland edge is the hypothetical inland limit of “substantial” mixing of end-member freshwater (salinity < 1PSU) and end-member saline groundwater (salinity ~35PSU) across the primary halocline. I was not able to observe or profile the inland edge of the mixing zone along the northern transect in the TRA. At the location Cenote Angelita, water column profiling revealed low salinity (0.9PSU) groundwater atop saline groundwater (~35PSU) with no visible mixed strata in between. Cenote Angelita is 22km from the coast and it is reasonable to think that the inland edge of the coastal mixing zone may be located between the coast and Cenote Angelita.
**The Bottom.** The bottom of the coastal mixing zone is easily located by water column profiling. The mixing zone bottom is the depth where the salinity of the groundwater becomes equal to, or possibly slightly greater than, the adjacent ocean (in TRA ~35PSU). There is usually a density boundary, or halocline, at this point. I refer to this halocline as the primary halocline and explain it in greater detail in Chapter 6.

**The Top.** The top of the mixing zone has two components: the *water table* and the *salinity step*. Near the coast, the mixing zone extends up to the water table. Further inland the top of the mixing zone does not extend all the way up to the water table, but is instead defined by a *salinity step* at depth. I set the uppermost boundary (whether at the water table or at the salinity step) at point where salinity increases above 1PSU. This is somewhat arbitrary, but 1PSU is the first substantial increase above the salinity values that were commonly measured in the Yucatan interior (~0.6 PSU).

**TRA Mixing Zone Morphology**

The morphology of the present day mixing zone in the TRA, as defined above, is shown in Figure 4.2.
Coastal Aquifers: The “Subterranean Estuary”

Moore (1999) made the connection between estuaries and their aquifer counterparts and coined the term “subterranean estuary” to describe these subterranean mixing zones. This term redefines thinking of coastal aquifers to acknowledge evidence of significant fresh/saline mixing in the subsurface and the importance of the chemical reactions that occur there.

The aquifer in the TRA functions as a hybrid between a normal estuary and a porous media aquifer. Extensive conduit systems are developed throughout the aquifer and allow for
rapid flow for freshwater toward the sea and for potential pathways for seawater intrusion. Some concepts from estuarine studies may be useful in studying this hybrid system.

**Mixing Evidence in Water Column Profiles**

In an estuary, the extent of mixing between overlying freshwater discharge and underlying saline water can be seen in plots of water column salinity (Pritchard, 1989). Pritchard’s water column profiles from estuaries (Fig. 4.3.) are strikingly similar to the profiles I created in the TRA (Fig 4.4).

![Figure 4.3](image1.png)  
**Figure 4.3.** Degree of mixing in an estuary revealed by water column profiles of salinity (after Pritchard, 1989).

![Figure 4.4](image2.png)  
**Figure 4.4.** Plots of water column salinity from three sites in the TRA. Note the similarity with Pritchard’s (1989) columns from estuaries. The ocean profile is from approximately 1km offshore from Tulum.
Mixing Induced Circulation?

Mixing of freshwater discharge with underlying saline water can lead to the production of a bottom current flowing into the estuary (Pritchard, 1989). This bottom current arises as saline water flows in to replace the volume of saline water entrained and discharged by mixing processes (Figure 4.5). Similar return current flows can be found in laboratory scale fluid mixing experiments (Keulegan, 1949; Silva and Fernando, 1998).

Figure 4.5. Estuary circulation (modified from Pritchard, 1989, 1955).

Given the evidence for extensive mixing revealed in many of the Yucatan water column profiles, and the flows induced by such mixing in estuaries and experiments, it seems likely that currents may be induced in the saline water by mixing processes in the TRA. This possibility clearly warrants further investigation.

Mixing Zone: Past

In order to assess the possible geologic impact of mixing zone processes over time, it is necessary to understand how the mixing zone has changed over time.
**Sea Level Change**

The primary factor affecting the position of the modern mixing zone is sea level. Sea level (and the related mixing zone) has only been at or above its present position for a small fraction of the recent geologic past (Imbrie *et al.*, 1984) (Figure 4.6). Over the last 750ka eustatic sea level has averaged around 60m below present (Imbrie *et al.*, 1984; Werner, 2001) (Figure 4.7). Past fluctuations in mixing zone position should be kept in mind if mixing zone processes are considered as a possible agent of wall-rock alteration in existing conduits or as an explanation for conduit initiation and growth.

**Mixing Zone Mobility**

Given the extent of sea level change in the past (Figure 4.6.), and the related migration of the mixing zone, one must be careful not to view the modern mixing zone as a static agent of geomorphologic change.

![Fig 4.6. Sea level over last 750ka. $\delta^{18}O$ record of Core DSDP 502b modified from Imbrie *et al.* (1984, fig. 5), with ordinate in meters derived from the $\delta^{18}O%$ variations in *Globigerinoides sacculifer* and abscissa the time in Ka BP. Modified from Werner, (2001).](image-url)
Past Mixing Zone Position

By using sea level curves in conjunction with topographic and bathymetric data it is possible to constrain the following: (i) where mixing zones may have been most active in the past, (ii) the approximate duration of activity of specific mixing zones, and (iii) the vertical range over which the mixing zone was active. However, before these sea level curves can be directly applied to the Yucatan, the tectonic stability of the Yucatan platform must be considered. The stability of the Yucatan platform is discussed in greater detail in Appendix I.

Stability Conclusions

The number of dated sea level indicators from the Yucatan is sparse (Coke, 1991 and Szabo et. al., 1979). Taken alone they weakly support the claim of tectonic stability in the Yucatan within the last 125ka. However, they are congruent with evidence one might expect to find on a stable coastline. The claim of tectonic stability in the northeastern Yucatan peninsula (within 125ka) is bolstered by the lack of any geomorphic evidence of significant vertical offset.
(e.g. raised marine terraces, fault scarps, etc.). Therefore, it seems reasonable to use eustatic sea-level curves in this study as long as the potential inaccuracies are recognized.

**Mixing Zone Migration in Recent Geologic Past**

Over the last ~125ka, sea level has varied over a range of more than 120m (Imbrie *et al.*, 1984). The Yucatan coastline has shifted in response to these variations in sea level and, because the mixing zone is directly related to the coastline position, the mixing zone has migrated substantially as well (Figures 4.8 and 4.9).

![Figure 4.8](image_url)

Figure 4.8. Plan View: Platform coastline at present and at the ~18ka sea level lowstand. This figure was created from the bathymetric data of Salvador (1991).
Figure 4.9. Profile View (A-A'): Platform exposure at present and at 18ka lowstand. This figure was created from bathymetric data of Salvador (1991).

**Duration of Mixing Zone activity in TRA**

The region where the modern TRA mixing zone is currently active has been exposed to coastal mixing processes for only a small fraction of the recent geologic past. This is an important fact to remember when looking for diagenetic evidence of the potentially corrosive effects of mixing.

The majority of the explored conduit systems presently explored in the TRA are less than 30m below present sea level. From the sea-level records outlined above and dated materials explained in Appendix I, I draw the following conclusions: (i) at ~125ka BP the conduits were inundated by the sea-level high stand and much of the modern mixing zone was subjected to
mixing processes similar to those occurring at present, and (ii) from ~18ka BP to at least ~8250 YBP the majority of conduits in the modern mixing zone were drained (and, therefore, in the vadose zone) and not subject to fresh/saline mixing processes. Thus, the bedrock in the modern mixing zone has been exposed to both phreatic and vadose weathering.
CHAPTER 5
MIXING BASICS

Introduction

In this chapter, I present an overview of the mixing processes and hydrogeochemical cycles that drive the mixing zone. I also outline the parameters, tracers, and functions that are useful in mixing zone studies. I present a more detailed discussion of mixing, as it actually occurs in the stratified TRA aquifer, in the following chapter.

Understanding the Mixing System

The study of any hydrogeochemical mixing system should begin with a rigorous definition of system processes, parameters, and rates. Specifically, it is necessary to understand the following:

(Note: the chapter or chapters covering each topic are given in parenthesis.)

1.) The overall hydrogeochemical cycle (this chapter)
2.) Identity of the mixing endmember solutions (this chapter)
3.) Chemical composition of each mixing member including parameters such as temperature, pH, and oxidation-reduction potential. (Chapter 2: Procedure and Chapter 7: Mixture Chemistry)
4.) The specific mechanisms that mix these members (this chapter and Chapter 6: Stably Stratified Flows)
5.) The rate and ratio of mixing (this chapter)

6.) The type and rates of chemical reactions resulting from mixing (Chapter 7: Mixture Chemistry)

7.) Composition, propagation, and fate of the resulting mixed solution (Chapter 6: Stably Stratified Flows)

This chapter addresses each of the above items in sequence.

**Hydrogeochemical Cycles**

Mixing of environmental fluids occurs over a wide range of scales and in countless, often interrelated, cycles. In the study of any particular mixing system, context is of paramount importance. The study of any mixing zone system should begin with a solid, fundamental understanding of these hydrogeochemical cycles before moving on to the identification of certain solutions as “representative” or as endmembers for geochemical reaction modeling.

**Cycle Stages**

The primary hydrogeochemical cycle of the TRA coastal mixing zone can be roughly divided into four steps or stages (Fig 5.1.): (i) separation, (ii) segregation, (iii) differentiation, and (iv) homogenization. This cycle continuously produces (through chemical differentiation) and destroys (through homogenization accomplished by mixing) water bodies that are heterogeneous (i.e. measurably different by some combination of chemical and/ or physical parameters). Each stage is explained in sequence below.
Figure 5.1. Primary hydrogeochemical cycle of a coastal mixing zone aquifer. The Separation stage is not exclusively accomplished by the evaporation of seawater. Numerous separation events may occur throughout the aquifer.

**Separation.** Two important separation events occur in the mixing zone cycle. The primary separation occurs as evaporation of seawater leads to subsequent precipitation of rain. This separation produces two distinct hydrologic members that may be crudely labeled as freshwater and seawater. Secondary separations may occur as seaward-flowing freshwater is divided by physical processes and/or aquifer heterogeneity. Examples of separation mechanisms
within an aquifer include the formation of stable stratification and the division of a fluid flow by an aquaclude or other physical constraints (Figure 5.2.).

*Figure 5.2.* Separation Mechanisms. Separation by evaporation-precipitation (A). Separation by aquifer heterogeneity (B). Separation by stratification (C).

**Segregation.** Once separated, waters must remain segregated for a significant period of time to allow differentiation by chemical and physical processes. In an aquifer, this segregation
may be maintained by the presence of aquacludes or formation of stable stratification. In the TRA, stratification is a very important and effective segregation mechanism as density differences between strata effectively suppress mixing.

**Differentiation.** Differentiation occurs as segregated waters are exposed to different chemical and physical environments. Differentiation in the TRA is accomplished by fluid-rock interactions and redox reactions.

**Homogenization.** Homogenization of heterogeneous groundwater flows is accomplished by a combination of dispersion and diffusion. In the TRA, this homogenization processes is rapidly accomplished by numerous physical mixing sites (like the Temple of Doom site explained later in this chapter). It is at this stage, Homogenization, that chemical mixing effects are initiated.

**Binary Mixing Systems**

Mixing of two solutions, or binary mixing, is the simplest mixing system to study and model. When more than two waters mix together, a slightly different and more complicated treatment is required. However, many complex mixing systems can be considered as simple, binary mixing systems if the scale (in both time and space) is restricted. This is my approach in dealing with the complex mixing systems in this study.

**End Members**

In a simple binary mixing scenario there are two solutions, known as end members, that are combined to form a new mixture. The study of any binary mixing system begins rather obviously with the identification of these mixing end members. In a natural environment, the
definition of end members may be quite arbitrary as there is no real starting point or end in a hydrogeochemical cycle. To meaningfully designate end-member solutions for the purposes of geochemical reaction modeling, it is necessary to define a hydrochemical cycle so that the end-member solutions can be placed in context.

**Composition of Mixing End Members**

Once the end members have been selected, they must be analyzed for various parameters. My approach to analysis was given in Chapter 2. The difficulties in this approach are explained in Chapter 8.

**Mixing Mechanisms**

Once the end members have been identified and analyzed, some consideration must be given to how these actually mix. Previous mixing zone studies have often focused on the geologic effects of chemical reactions that occur after mixing (Plummer *et. al.*, 1976; Smart *et. al.*, 1988; Mylorie and Carew, 1990). Comparatively, those in the geologic/ hydrogeologic community have given comparatively little attention to the mechanisms that cause mixing. In contrast, other disciplines (*e.g.* environmental engineering, oceanography, and limnology) have given great attention to mixing between stratified fluids and have developed useful tools for application in mixing studies. A common approach among hydrogeologists is to select some inland water as the “freshest” end member, select local seawater as the other mixing end member, and then simply presume that somehow the two must mix within the area of study.

**Dispersion, Diffusion, and Double Diffusive Convection**

Mixing may be accomplished by three processes: (i) turbulent physical mixing (dispersion), (ii) diffusion, and (iii) double diffusive convection. In the TRA mixing zone,
diffusion appears to be subordinate to physical mixing in many locations. Double diffusive convection may operate in the TRA coastal mixing zone, but I have no direct evidence that it does.

**Turbulent Mixing at the Temple of Doom**

The Temple of Doom site is a centerpiece of my study and is an excellent location for the study of mixing processes. At the Temple of Doom site I found a vent-like feature that forces mixing between the saline groundwater (salinity ~ 35PSU) and overlying freshwater (salinity of 3 PSU). The large density difference between these two waters is a very effective segregation mechanism prior to forced mixing.

**Mixing Ratio and Flux**

Once end members have been identified (and it has been established that they are mixed by some mechanism) it is time to move to the next level of detail; establishing the ratio and flux of mixing. Quantification of mixing rates and flux is important in assessing the geologic significance of mixing effects. If a solution becomes highly aggressive by mixing, but only a very small volume is produced, the geologic impact will likely be small. However, if a marginally aggressive mixed solution is produced in very large volumes, it may have a more significant effect.

**Flux**

Flux is the rate of flow of mass, volume, or solute concentration per cross-sectional area per time. Mixing by turbulent physical mixing, as is common in the TRA mixing zone, may produce a larger flux of mixed solution than simple (and slow) diffusion.
Mixing Rates and Chemical Kinetics

The rate of fluid mixing may affect the chemical reactions that occur in the mixed solution. Ionic reactions occur within milliseconds while some redox reactions may take several minutes or hours to reach equilibrium (Millero, 2001). Consequently, slow mixing through diffusion may allow time for ionic and redox reactions to reach equilibrium, whereas rapid turbulent mixing may quickly flush the mixed water away from the mixing site before redox reactions can attain equilibrium.

Mixing Ratios and Percentages

Plummer (1975) demonstrated that the saturation index of a newly mixed solution is not only a function of the initial chemical composition of the end-member solutions, but it is also affected by the ratio at which the two-endmembers are mixed. Given that the mixing ratio is so important, how can it be quantified at mixing sites in the TRA?

Mixing Ratio Determined by Conservative Tracer

Mixing ratios can be calculated by measuring the concentration of a conservative tracer, such as chloride, in both mixing end-members and in the resulting mixed fluid (Langmuir, 1997). Wide variations in salinity (and related chloride concentration) across the TRA makes chloride an ideal tracer for this study. The equation relating a conservative tracer to mixing ratio is given below (Equation 5.1) (Langmuir, 1997). C denotes ion concentration, V denotes volume, and subscripts 1, 2, and m indicate end-member 1, end-member 2, and mixture respectively.

\[
R = \frac{V_1}{V_2} = \frac{(C_2 - C_m)}{(C_m - C_1)}
\]

(5.1)
Mixing Ratio Determined by Salinity

Salinity is one of the most commonly recorded parameters in mixing zone studies. Total salinity ($S_T$), defined as a mass ratio, is conservative and linear (see Appendix G for more on salinity). Therefore, salinity can be used to determine mixing ratios although perhaps with less accuracy than chloride concentrations.

Because salinity is most commonly calculated from the electrical conductivity of solutions, and not directly calculated from a total water analysis, it is subject to some complicating factors. Electrical conductivity of various solution mixtures may not be linear and consequently may lead to inaccuracies if it used to calculate mixing ratios. Despite its limitations, salinity (as determined from conductivity) is very convenient to use and should be reasonably accurate as long as the limitations are kept in mind.

Total salinity can be used to easily calculate mixing ratios by equations 5.2 and 5.3.

\[
(5.2) \quad \frac{(S_{\text{mix}} - S_{\text{fresh}})}{(S_{\text{saline}} - S_{\text{mix}})} = \text{mixing (by mass) ratio}
\]

\[
(5.3) \quad \left[ \frac{(S_{\text{mix}} - S_{\text{fresh}})}{(S_{\text{saline}} - S_{\text{mix}})} \right] \times 100 = \text{mixing (by mass) percentage}
\]

A chart produced from this equation for use specifically in the TRA is reported in Appendix L: Mixing Ratio Chart.
CHAPTER 6
STABLY STRATIFIED FLOWS

Introduction
The aquifer in the TRA is stratified by density into stable flows. The presence of stratification in this aquifer has been known for some time (Back and Handshaw, 1970). Stratification in the TRA is more complex than in an idealized aquifer system with a single “freshwater lens” floating atop saline groundwater. This chapter explains the state of stratification in the TRA, the origin and fate of strata, and the impact of stratification on mixing and mixing chemistry.

Evidence of Stratification in TRA
In the TRA, there is an uppermost lens of low salinity, in most cases overlying one or more units of slightly greater salinity. Ultimately there is a density interface, below which the groundwater salinity is very near that of seawater (35PSU or above; Figure 6.1). I define this boundary as the primary halocline. Other subordinate haloclines may be present higher in the water column above the primary halocline.
In the TRA, these strata are well defined by the use of the MiniSonde 4 multi-parameter probe and by using the profiling methods outlined in Chapter 2. The water column profiles obtained with the MiniSonde 4 show marked differences in chemical and physical parameters (such as pH, temperature, and dissolved oxygen) with change in depth (Figure 6.2). Strata can be effectively mapped by creating a series of water column profiles along a transect (Esterson, 2002).
Origin of Stratification

During my fieldwork in the TRA, I found four physical mixing sites that blend fresh and saline groundwater. Because water density is primarily a function of salinity (see Figure M.2. in Appendix M), this mixing creates discrete flows, or lenses, of intermediate density. Through numerous mixing events, the TRA aquifer has become complexly stratified.

Growth and Propagation of the Mixed Lens

If two stratified flows should mix, the resulting mixed solution will have a density intermediate between the densities of the two original flows. If the density differences between
these solutions are large enough, and flow velocities are low enough, the mixed solution may stabilize into a new unit located between the two original strata.

For example, if the lowermost saline groundwater unit mixes with overlying freshwater, it will produce a third, brackish stratum. This brackish, mixed lens forms above the primary halocline (Figure 6.3.). With each mixing event the uppermost mixing interface moves upward. Eventually, this interface reaches the water table. This point aids in the delineation of the coastal mixing zone morphology as explained in Chapter 4.

![Diagram of mixed lenses](image)

Figure 6.3. Upward growth of mixed lenses in profile view. The mixed lens grows between its “parent” strata.

**Morphology and Behavior of a Mixed Lens**

A mixed lens is defined by density interfaces that form upper and lower boundaries. Once produced, a mixed lens may remain stable and propagate for significant distances though the aquifer. For example, the mixed lens created at the TRA Temple of Doom site stabilizes into a discrete lens that can be traced through conduits for more than 0.5km as it flows toward the
Caribbean Sea (Esterson, 2002). If the mixed lens is aggressive (undersaturated with respect to calcite), it can be viewed as a geochemically reactive plume.

**Segregation by Stratification**

Density stratification also effectively *segregates* water masses by limiting vertical mixing across the density boundary (the geochemical importance of segregation is explained in Chapter 5: Mixing Basics). The effectiveness of the density interfaces in limiting vertical mixing can be seen in the sharp changes in parameters such as dissolved oxygen or salinity as a function of depth (Figure 6.4).

![Salinity and pH profiles](image)

Figure 6.4. Sharp boundaries across density interface between strata. Note that the change in pH and salinity is step-like and not gradational. Profile is from Cenote Angelita.
Implications for Mixing Corrosion

Bogli (1964) envisioned mixing, and mixing corrosion, occurring at conduit junctions where flows converged. His idea implies that conduit walls segregate heterogeneous waters. However, in areas with stratified flows and permeable limestone bedrock the mixing situation may be quite different.

In the TRA, conduit walls, and the limestone bedrock that forms them, are often very porous and highly permeable. Consequently, conduit walls may not be very effective in maintaining segregation of waters. However, segregation may result from the presence of density interfaces. In stratified flows, mixing occurs across planar, horizontal density interfaces (Figure 6.5) and not necessarily only at conduit junctions.

Figure 6.5  Mixing of non-stratified waters at lateral conduit junctions (A) versus vertical mixing across density interfaces (B). Conduits are shown in profile view.
Mixing Across Density Interfaces in TRA

In the TRA, the greatest potential for significant mixing corrosion may not be at lateral conduit junctions, but at sites where vertical mixing across density boundaries occurs. Mixing does take place at conduit junctions, but as a result of the high permeability of the limestone matrix (and extensive inter-connected nature of conduits) the conduit flows may not be well segregated laterally. As a consequence of this poor segregation, there may be little chemical heterogeneity in the two mixing waters and, hence, little potential for significant mixing corrosion. In contrast, the mixing of stratified flows must involve mixing of significantly heterogeneous waters (the flows must be physico-chemically heterogeneous to create stratification).
CHAPTER 7
MIXTURE CHEMISTRY

Introduction
As explained in previous chapters, the aquifer of the Tulum Research Area (TRA) is an area of intense physical mixing between freshwater and saline groundwater. The mixing of these two physico-chemically heterogeneous waters can affect the key parameters of the carbonate system. The mixing-induced chemical effects that relate to the carbonate system may be referred to collectively as “mixing effects” (Ford and Williams, 1989). This chapter explains these mixing-induced chemical effects as they relate to the carbonate system and to the primary hypothesis of this thesis.

Carbonate System
The freshwater flowing seaward Yucatan peninsula is often saturated with calcite and is dominated by the carbonate system (Back et. al, 1986; Back and Handshaw, 1970). In the Tulum Research Area (TRA) coastal mixing zone, this freshwater body mixes with saline groundwater (geochemically modified seawater). Seawater (and the geochemically modified saline groundwater that is derived from it) has a well-studied carbonate system (DOE, 1994; Millero, 1996). The carbonate system can be quantified by measurement of any two of the following parameters: total alkalinity, total dissolved inorganic carbon, total hydrogen ion concentration (i.e. pH), and fugacity of CO$_2$ (DOE, 1994).
Theoretical Foundation

The landmark papers of Bogli (1964) and Plummer (1975) form the theoretical foundation of my study. Bogli examined the reactions of the carbonate system at conduit junctions in freshwater karst systems (Bogli, 1964). The mixing solutions in Bogli’s work had two primary geochemical variables: partial pressure of carbon dioxide ($P_{CO_2}$) and to a lesser degree, temperature. Plummer (1975) expanded his work to include mixing of waters with various salinities. Thus the reactions explained by Plummer had three primary variables: salinity (or ionic strength), $P_{CO_2}$, and temperature. It should be noted that fugacity of CO$_2$ has replaced $P_{CO_2}$ in most recent studies (DOE, 1994; Millero, 2001; Millero, 1996).

Geochemical Effects of Mixing

Numerous geochemical effects take place upon mixing (Thrailkill, 1968; Runnels, 1969). Ford and Williams (1989) published one of the most comprehensive lists of mixing effects that may affect the carbonate system as it relates to mixing corrosion. These effects include: (i) the foreign ion effect (also referred to as the ionic strength effect), (ii) the temperature effect, (iii) the common ion effect, and (iv) the $\Delta P_{CO_2}$ effect envisioned by Bogli (1964). The foreign ion effect and $\Delta P_{CO_2}$ effect are potentially the most dominant effects in the TRA and are explained further in this chapter.

The common ion effect is not a dominant effect in the TRA mixing zone. The temperature effect is rather limited in the Yucatan given its tropical latitude and small temperature difference between mixing water masses (commonly within 1.5°C). The common ion and temperature effects are incorporated into the geochemical modeling calculations of PHREEQC but are not explained in detail here.
**Foreign Ion/ Ionic Strength Effect**

This effect suppresses ion activity by the addition of ions outside the carbonate system (hence the designation as “foreign ions”). This effect is very important where waters of varying salinities mix (i.e. coastal mixing zones). These foreign ions include Mg$^{2+}$, Na$^+$, K$^+$, and Cl$^-$. Suppression of Ca$^{2+}$ ion activity by the foreign ion effect changes the saturation index of calcite for a given solution, and may lead to mixing corrosion in some cases. Plummer (1975) explored this possibility in detail.

**Δ$P_{CO2}$ Effect**

The Δ$P_{CO2}$ effect as envisioned by Bogli (1964) operates when two waters, each saturated with respect to calcite but varying in $P_{CO2}$ (or similarly CO$_2$ fugacity), mix to produce a newly aggressive solution that is undersaturated. In the TRA, calcite often rapidly precipitates when groundwater comes in contact with the atmosphere. This is an indication that the groundwater is often saturated with respect to calcite and that mixing corrosion as envisioned by Bogli (1964) should be possible in some instances.

**Temperature Effect**

Calcite solubility decreases with increasing temperature (Langmuir, 1997). Carbon dioxide gas solubility also decreases with increasing temperature thereby increasing the magnitude of the temperature effect (Langmuir, 1997). In the TRA mixing zone, the temperature variation between mixing members is rarely more than 1.5 C making the temperature effect relatively unimportant compared to the foreign ion effect and Δ$P_{CO2}$ effect.
Reaction Complexity and PHREEQC

The geochemical modeling program PHREEQC is capable of resolving each of these mixing effects simultaneously (Parkhurst and Appelo, 1999). Separating the mixing induced reactions into individual effects was done to guide the selection of endmembers to be collected in the field and to enhance understanding of the relative magnitude of each of the effects.
CHAPTER 8
RESULTS AND DISCUSSION

Introduction

This section is organized into the following sections: (i) water column profiling, (ii) ion analysis, and (iii) aqueous geochemical modeling.

Water Column Profiling

The water column profiling plan produced . A selected, representative group of water column profiles can be found in Appendix B. Annotated versions of especially interesting columns are in Appendix A. The water column profiles provide evidence of the following:

1.) The water column is often stratified by salinity (and thus density).

2.) The interface between strata is sharp, not gradational.

3.) There is considerable mixing between density strata at certain locations.

4.) Mixing, as it relates to mixing corrosion, occurs across density interfaces, not just at conduit junctions.

5.) Stratification is effective in suppressing mixing and thus promotes segregation of chemically heterogeneous water flows.
Ion Analysis

Cation Analysis

Cation analysis by ICP-MS did not return data of adequate accuracy for use in aqueous geochemical modeling (see Appendix D for details). Determination of calcium (the single most critical measurement in determining saturation indices for calcite) was especially problematic. The variation in sample salinity led to non-linear behavior during ICP-MS analysis. Calcium was not only non-linear in the higher salinity samples, but the detection (in counts per second) of calcium ions actually decreased with increasing concentration in some samples. This makes the use of standard addition inappropriate.

Anion Analysis

Anion analysis by ion chromatography was successful and the results are displayed in Appendix E.

Results from Ion Analysis

The results of the cation analysis by ICP-MS were of inadequate accuracy for use in PHREEQC modeling. To fix this problem, the method could possibly be altered to include a dilution scheme that would bring all samples to nearly the same ionic strength before injection into the ICP-MS. The creation of ion specific calibration curves might be another solution. However, with the limited time and funding available, I did not have the opportunity to attempt these method alterations. New advances in ion chromatography equipment and methods seem to offer a more robust and cheaper alternative for cation analysis.
Aqueous Geochemical Modeling

Without adequately accurate cation results, aqueous geochemical modeling using PHREEQC was not possible. Consequently, my procedure (as outlined in Chapter 2) was terminated at this stage.
CHAPTER 9
CONCLUSION

Primary Hypothesis

The primary hypothesis was not significantly supported by my investigative approach. Analytical difficulties in the lab prevented me from getting data accurate enough to calculate meaningful saturation indices using the geochemical modeling program PHREEQC. Without these saturation index calculations it was impossible to determine if undersaturated waters are produced by mixing processes in the TRA mixing zone. However, as a result of this investigation I have been able to move forward in defining the mixing zone system, in identifying key parameters that quantify the system, and in building a foundation for future investigation of interesting coastal mixing zone processes.
APPENDIX A

ANNOTATED WATER COLUMN PROFILES
Active physical mixing along irregular vent ceiling

Discharge is mixture of fresh/saline waters

Reduced DO, but not anoxic

Casa Cenote:
Column A  7-01-2001
Cenote Azul:
Column B  7-07-2001
Cenote Calimba:
Column B 8-22-2000
Cenote Zaci:
Column B 7-05-2001
only slight increase in temp

no mixed zone

pH spike at boundary, then return to alkaline

Naharon:
Column B  8-17-2000
gradual shift in temp

halocline 1

Mixed zone ~2m thick

halocline 2

'saline'

Mixed zone ~2m thick

~2m thick mixed zone

lowest pH in mixed zone

alkaline pH shift in saline water

DO (mg/L)

Mayan Blue:
Column B  8-20-2000
little change in temp

mixed zone

'saline'

'saline'

no oxygen consumption

slightly lower pH

Sistema Tortuga:
Column A  8-24-2000
Sistema Tortuga:
Column C  8-24-2000
Temple of Doom:
Column B  8-23-2000
Temple of Doom:  
Column B  7-02-2001
thermocline

Temp

Depth (m)

0 10 20 30 40 50 60

16.0

15.5

15.0

14.5

14.0

13.5

13.0

0 10 20 30 40 50 60

16.0

15.5

15.0

14.5

14.0

13.5

13.0

SpC (mS/cm)

halocline

Salinity

Reduction of saline mixing end-member to pH 7.2 enhances potential of mixing effects dissolution

Salinity < 2.5 ppt indicates water has not mixed significantly with underlying saline water

sharp halocline without mixed zone or evidence of significant diffusion across boundary

Salinity= ~35 ppt
Same as seawater

Reduction of oxygen, but still oxic

Temple of Doom:
Column E  7-02-2001

DO (% Saturation)
Lower pycnocline within 10cm of 2000 position

Mixed Zone 2.2m Thick

Slight ‘pooling’ of higher salinity water near lower pycnocline

Lowered pH in mixed zone

Reduced oxygen below 1st halocline, but oxic throughout

Temple of Doom:
Column N  7-03-2001
APPENDIX B

WATER COLUMN PROFILES
Caribbean Sea off Tulum:
Column B  6-29-2001
Cenote Angelita:
Column A  8-24-2000
Cenote Angelita:
Column B  8-24-2000
Cenote Azul:
Column A  7-07-2001
Cenote Azul:
Column B  7-07-2001
Casa Cenote:  
Column A  7-01-2001
Casa Cenote:
Column B   7-01-2001
Cenote Calimba:
Column A  8-22-2000
Cenote Calimba:  Column B  8-22-2000
Cenote Carwash:
Column A  8-21-2000
Cenote Carwash:
Column B  8-21-2000
Cenote Carwash: Column D  8-21-2000
Cenote Conquistador:
Column A  6-30-2001
Cenote Conquistador:
Column B  6-30-2001
Cenote del Mar:
Column A  8-19-2000
Cenote del Mar:
Column B  8-19-2000
Cenote del Mar:
Column C  8-19-2000
Cenote del Mar:
Column D  8-19-2000

No Dissolved Oxygen Record
Cenote Samula:
Column A  6-22-2001
Cenote Samula:
Column B  6-22-2001
Cenote Zaci: 7-05-2001

Column A
Cenote Zaci:
Column B  7-05-2001
Gran Cenote:
Column A  8-16-2000
Mayan Blue:
Column A  8-20-2000
Mayan Blue:
Column B  8-20-2000
Mayan Blue:
Column C  8-20-2000
Naharon:
Column A  8-17-2000
Naharon:
Column B  8-17-2000
Naharon:
Column C  8-17-2000
Sistema Tortuga:
Column B  8-24-2000
Sistema Tortuga:
Column C  8-24-2000
Temple of Doom:
Basin Column  8-23-2000
Temple of Doom: Basin Column II 8-25-2000
Temple of Doom:
Column A  8-23-2000
Temple of Doom:
Column B  8-23-2000
Temple of Doom:
Column C  8-25-2000
Temple of Doom:
Column D  8-25-2000
Temple of Doom:
Column A 7-02-2001
Temple of Doom:
Column B  7-02-2001
Temple of Doom:
Column C  7-02-2001
Temple of Doom:
Column D 7-02-2001
Temple of Doom:
Column E  7-02-2001
Temple of Doom:
Column F  7-03-2001
Temple of Doom:
Column G    7-03-2001
Temple of Doom:
Column H  7-03-2001
Temple of Doom:
Column I   7-03-2001
Temple of Doom:
Column J  7-03-2001
Temple of Doom:
Column K  7-03-2001
Temple of Doom:
Column L  7-03-2001
Temple of Doom: Column M 7-03-2001
Temple of Doom:
Column N  7-03-2001
APPENDIX C

SAMPLE LOG
Table C.1. Water sample log from TRA 2000 field season. Each entry has a site name (i.e. Temple of Doom), a location given in latitude and longitude, a sample number that corresponds to the site name (i.e. TD1), and a description of the type and location of each sample.

Temple of Doom (TD)  20 13 45N 087 27 26W

“Vent” refers to a specific mixing site approximately 100m upstream from cenote basin.

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD1</td>
<td>Saline</td>
<td>Saline water from below Vent</td>
</tr>
<tr>
<td>TD2</td>
<td>Mixed</td>
<td>At mixing boundary below Vent</td>
</tr>
<tr>
<td>TD3</td>
<td>Fresh</td>
<td>Freshwater just before mixing in Vent</td>
</tr>
<tr>
<td>TD4</td>
<td>Mixed</td>
<td>From mixed zone (12.2m -14.0m depth), near cavern</td>
</tr>
<tr>
<td>TD5</td>
<td>Fresh</td>
<td>Freshwater just before mixing in Vent</td>
</tr>
<tr>
<td>TD6</td>
<td>Saline</td>
<td>Saline water from below Vent</td>
</tr>
<tr>
<td>TD7</td>
<td>Fresh</td>
<td>Freshwater just before mixing in Vent</td>
</tr>
<tr>
<td>TD8</td>
<td>Saline</td>
<td>Saline water from below Vent</td>
</tr>
</tbody>
</table>

Grand Cenote (GC)  20 14 47N 087 27 52W

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC1</td>
<td>Saline</td>
<td>Saline water from below Vent</td>
</tr>
<tr>
<td>GC2</td>
<td>Mixed</td>
<td>At mixing boundary below Vent</td>
</tr>
<tr>
<td>GC3</td>
<td>Fresh</td>
<td>Freshwater just before mixing in Vent</td>
</tr>
</tbody>
</table>

Cenote Del Mar (DM)  20 09 14N 87 27 27W

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM1</td>
<td>Fresh</td>
<td>Above both haloclines</td>
</tr>
<tr>
<td>DM2</td>
<td>Saline</td>
<td>Warm seawater at lowest passage level</td>
</tr>
<tr>
<td>DM3</td>
<td>Fresh</td>
<td>Freshwater just before mixing in Vent</td>
</tr>
<tr>
<td>DM4</td>
<td>Mixed</td>
<td>From mixed zone between 12.2m and 14.0m depth</td>
</tr>
</tbody>
</table>

Mayan Blue (MB)  20 11 37N 087 29 47W

<table>
<thead>
<tr>
<th>Number</th>
<th>Type</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB1</td>
<td>Mixed</td>
<td>Just below first halocline</td>
</tr>
<tr>
<td>MB2</td>
<td>Saline</td>
<td>Below last halocline</td>
</tr>
<tr>
<td>MB3</td>
<td>Fresh</td>
<td>Freshwater well above halocline</td>
</tr>
</tbody>
</table>
Table C.1. (Continued from previous page). Water sample log from TRA 2000 field season.

<table>
<thead>
<tr>
<th>Location</th>
<th>20 16 38N 087 28 34W</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tortuga (TT)</strong></td>
<td></td>
</tr>
<tr>
<td>Number</td>
<td>Type</td>
</tr>
<tr>
<td>TT1</td>
<td>Fresh</td>
</tr>
<tr>
<td>TT2</td>
<td>Fresh</td>
</tr>
<tr>
<td>TT3</td>
<td>Saline</td>
</tr>
<tr>
<td><strong>Abejas (AB)</strong></td>
<td>20 13 59N 087 25 18W</td>
</tr>
<tr>
<td>Number</td>
<td>Type</td>
</tr>
<tr>
<td>AB1</td>
<td>Fresh</td>
</tr>
<tr>
<td>AB2</td>
<td>Saline</td>
</tr>
<tr>
<td><strong>Carwash (CW)</strong></td>
<td>20 16 28N 087 29 11W</td>
</tr>
<tr>
<td>Number</td>
<td>Type</td>
</tr>
<tr>
<td>CW1</td>
<td>Fresh</td>
</tr>
<tr>
<td>CW2</td>
<td>Fresh</td>
</tr>
<tr>
<td>CW3</td>
<td>Fresh</td>
</tr>
<tr>
<td><strong>Cenote Cristal/Naharon (CC)</strong></td>
<td></td>
</tr>
<tr>
<td>Number</td>
<td>Type</td>
</tr>
<tr>
<td>CC1</td>
<td>Fresh</td>
</tr>
<tr>
<td>CC2</td>
<td>Mixed/Saline</td>
</tr>
<tr>
<td>CC3</td>
<td>Fresh</td>
</tr>
<tr>
<td>CC4</td>
<td>Saline</td>
</tr>
<tr>
<td><strong>Cenote Calimba/Azteca (CL)</strong></td>
<td>20 15 03N 087 28 02W</td>
</tr>
<tr>
<td>Number</td>
<td>Type</td>
</tr>
<tr>
<td>CL1</td>
<td>Fresh</td>
</tr>
<tr>
<td>CL2</td>
<td>Fresh</td>
</tr>
</tbody>
</table>
APPENDIX D

CATION ANALYSIS BY ICP-MS
Method

Instrument

I used a Finnegan Element 1 inductively-coupled plasma mass spectrometer (ICP-MS) to determine cations in the Yucatan samples. The samples were analyzed for Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$. This method was modified from Field et al., (1999).

Sample Preparation

Samples were filtered using a 0.2 μm Polysulfone Acrodisc® syringe filter. The filtered samples were then divided into three subsamples and each subsample was weighed. For increased accuracy, all dilutions and spike preparations were done by weight and not by volume.

Standard Addition

To calibrate the ICP-MS, I used standard addition of each cation (Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$ and Sr$^{2+}$).

Sequence

The autosampler capacity was twenty-four samples per tray. Four sampling sessions were required to run all 93 samples. The samples and standards were run in the following order:

1. Blank
2. Na Standard 300ppb
3. Na Standard 3ppm
4. Sample 1- without standard addition
5. Sample 1- with 1st standard addition
6. Sample 1 - with 2nd standard addition
7. Sample 2 - without standard addition
8. Sample 2 - with 1st standard addition
9. Sample 2 - with 2nd standard addition
10. Sample 3 - without standard addition
11. Sample 3 - with 1st standard addition
12. Sample 3 - with 2nd standard addition
13. Blank
14. Na Standard 300ppb
15. Na Standard 3ppm
16. Sample 4 - without standard addition
17. Sample 4 - with 1st standard addition
18. Sample 4 - with 2nd standard addition
19. Sample 5 - without standard addition
20. Sample 5 - with 1st standard addition
21. Sample 5 - with 2nd standard addition
22. Sample 6 - without standard addition
23. Sample 6 - with 1st standard addition
24. Sample 6 - with 2nd standard addition
25. Blank
26. Na Standard 300ppb
27. Na Standard 3ppm
28. Sample 7 - without standard addition
Matrix Effects

The samples ranged in salinity from approximately 1 to 35PSU. Matrix effects in the higher salinity samples became a concern. For this reason, I did not add sodium to the standard addition spike. To do so would have only increased the problems associated with higher ionic strength samples. Instead, sodium was determined by comparing the samples to independent sodium standard solutions of 3ppm and 0.3ppm (actually 2.97ppm and .297ppm).

Sodium Analysis

**Na Standards.** Sodium standards were prepared to near 3ppm and 0.3ppm.

Na 3ppm: \[ \frac{0.149g \text{ 1000ppm Na}}{50.109g \text{ total wt}} = 2.9735 \text{ ppm} \]
Na 0.3ppm: \[ \frac{1.503 \text{ 10ppm}}{50.421g \text{ total wt}} = 0.29789 \text{ ppm} \]
The sodium sample results were graphed to produce a slope-intercept equation relating counts/second to parts-per-million. The equation has the form $y = mx + b$, where $y = \text{Na (ppm)}$ and $x = \text{counts/second}$. The sodium analysis is shown in Figure D.1.

![Graphs of Na standards](image)

Figure D.1. Na standards. Counts per second (cps) versus ppm.

Equations used to calculate actual Na in ppm from raw data:

- Sample Round 1: $y = 6E-06x - 0.0111$ \( R^2 = 0.9979 \)
- Sample Round 2: $y = 4E-06x - 0.0169$ \( R^2 = 0.9998 \)
- Sample Round 3: $y = 6E-06x - 0.0142$ \( R^2 = 0.9978 \)
- Sample Round 4: $y = 6E-06x - 0.02$ \( R^2 = 0.9993 \)
K, Ca, Mg, and Sr Analysis

Spikes. Several spikes were created for standard addition into each sample run.

The spikes include:

- Spike A: Contained K, Ca, Mg, Sr, and In
- Spike C: Contained K, Ca, Mg, Sr, and In

Spike A was the lower concentration standard and Spike C was the higher concentration standard. Two spike series were created: one for saline samples and one for fresh samples.

These details of these spikes are displayed in Table D.1.

### Table D.1. Composition of spikes used in standard addition method.

<table>
<thead>
<tr>
<th>Spikes</th>
<th>10ppm K</th>
<th>10ppm Ca</th>
<th>10ppm Mg</th>
<th>10ppm Sr</th>
<th>1ppm In</th>
<th>0.009734 Spike wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fresh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spike A</td>
<td>total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ideal</td>
<td>by wt (g)</td>
<td>0.05</td>
<td>2.2</td>
<td>4.4</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>actual</td>
<td>by wt (g)</td>
<td>x</td>
<td>2.103</td>
<td>4.417</td>
<td>1.091</td>
<td>1.107</td>
</tr>
<tr>
<td></td>
<td>fraction</td>
<td>0.1926</td>
<td>0.404524</td>
<td>0.099918</td>
<td>0.101383</td>
<td>0.201575</td>
</tr>
<tr>
<td>ppm in final</td>
<td>1.926001</td>
<td>4.045242</td>
<td>0.999176</td>
<td>0.101383</td>
<td>0.001962</td>
<td></td>
</tr>
<tr>
<td>Spike C</td>
<td>total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ideal</td>
<td>by wt (g)</td>
<td>11</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>actual</td>
<td>by wt (g)</td>
<td>11.084</td>
<td>10.999</td>
<td>2.226</td>
<td>2.271</td>
<td>2.158</td>
</tr>
<tr>
<td></td>
<td>fraction</td>
<td>0.385691</td>
<td>0.382734</td>
<td>0.077458</td>
<td>0.079024</td>
<td>0.075092</td>
</tr>
<tr>
<td>ppm in final</td>
<td>3.856914</td>
<td>3.827337</td>
<td>0.774584</td>
<td>0.079024</td>
<td>0.000731</td>
<td></td>
</tr>
</tbody>
</table>

| Spike A | Spike C |         |         |         |        |                  |
|         |         |         |         |         |        |                  |
| saline  | saline  |         |         |         |        |                  |
| Spike A | total   |         |         |         |        |                  |
| ideal  | by wt (g) | 12      | 6       | 1.2     | 1.2    | 1.2              | 1.2                |
| actual | by wt (g) | 12.011  | 5.985   | 1.203   | 1.178  | 1.199            | 21.576             |
| | fraction | 0.556683| 0.277392| 0.055756| 0.054598| 0.055571        |
| ppm in final | 5.566834  | 2.773915 | 0.557564 | 0.054598 | 0.000541 |

| Spike C | total   |         |         |         |        |                  |
|         |         |         |         |         |        |                  |
| saline  | saline  |         |         |         |        |                  |
| Spike C | total   |         |         |         |        |                  |
| ideal  | by wt (g) | 24      | 12      | 1.8     | 1.8    | 1.2              | 1.2                |
| actual | by wt (g) | 23.981  | 11.96   | 1.814   | 1.786  | 1.371            | 40.912             |
| | fraction | 0.586161| 0.292335| 0.044339| 0.043655| 0.033511        |
| ppm in final | 5.861605  | 2.923348 | 0.443391 | 0.043655 | 0.000326 |
Non-linearity

The method of standard addition requires that the mass spectrometer detector have linear (or nearly linear across a restricted range) response to variations in sample ion concentration. This was not true for all cations that I analyzed. Sodium was nearly linear (Figure D.1). However the other cations showed significant nonlinear behavior (Figures D.2 and D.3).
Figure D.2. All cations. Counts per second (cps) versus ppm. Note that the ‘tiered’ nature of the detector response indicates a non-linearity that makes the use of standard addition invalid.
Figure D.3. Magnesium values of a typical saline and fresh sample. CPS versus ppm in a saline sample compared to a fresh sample. Note that in the saline sample setting the regression line y-intercept to zero gives a very poor fit.
APPENDIX E

ANION ANALYSIS
Table E.1. Results of anion determination by ion chromatography. Chloride and sulfate in millimoles (mM).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Chloride (mM)</th>
<th>Sulfate (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td>546.27</td>
<td>28.271</td>
</tr>
<tr>
<td>AB1</td>
<td>67.518</td>
<td>4.2856</td>
</tr>
<tr>
<td>AB2</td>
<td>541.22</td>
<td>27.757</td>
</tr>
<tr>
<td>CC1</td>
<td>45.2</td>
<td>3.107</td>
</tr>
<tr>
<td>CC2</td>
<td>415.09</td>
<td>22.684</td>
</tr>
<tr>
<td>CC3</td>
<td>19.252</td>
<td>1.2497</td>
</tr>
<tr>
<td>CC4</td>
<td>524.92</td>
<td>27.079</td>
</tr>
<tr>
<td>CL1</td>
<td>14.536</td>
<td>0.87468</td>
</tr>
<tr>
<td>CL2</td>
<td>14.281</td>
<td>0.9433</td>
</tr>
<tr>
<td>CW1</td>
<td>10.779</td>
<td>0.81013</td>
</tr>
<tr>
<td>CW2</td>
<td>3.4355</td>
<td>0.037342</td>
</tr>
<tr>
<td>CW3</td>
<td>10.526</td>
<td>0.0001</td>
</tr>
<tr>
<td>DM1</td>
<td>66.971</td>
<td>4.1469</td>
</tr>
<tr>
<td>DM2</td>
<td>427.28</td>
<td>22.662</td>
</tr>
<tr>
<td>GC1</td>
<td>16.039</td>
<td>1.1423</td>
</tr>
<tr>
<td>GC2</td>
<td>16.2</td>
<td>1.0945</td>
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<tr>
<td>MB1</td>
<td>346.81</td>
<td>17.651</td>
</tr>
<tr>
<td>MB2</td>
<td>529.72</td>
<td>27.111</td>
</tr>
<tr>
<td>MB3</td>
<td>20.628</td>
<td>1.4729</td>
</tr>
<tr>
<td>SG1</td>
<td>8.7719</td>
<td>1.8181</td>
</tr>
<tr>
<td>SS1</td>
<td>17.612</td>
<td>2.4797</td>
</tr>
<tr>
<td>TD1</td>
<td>547.29</td>
<td>27.761</td>
</tr>
<tr>
<td>TD2</td>
<td>148.5</td>
<td>8.6848</td>
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<tr>
<td>TD3</td>
<td>45.36</td>
<td>2.8518</td>
</tr>
<tr>
<td>TD4</td>
<td>156.19</td>
<td>8.8263</td>
</tr>
<tr>
<td>TD5</td>
<td>67.773</td>
<td>4.3601</td>
</tr>
<tr>
<td>TD6</td>
<td>531.37</td>
<td>27.471</td>
</tr>
<tr>
<td>TD7</td>
<td>61.67</td>
<td>3.9779</td>
</tr>
<tr>
<td>TD8</td>
<td>542.02</td>
<td>27.663</td>
</tr>
<tr>
<td>TT1</td>
<td>3.9272</td>
<td>0.12099</td>
</tr>
<tr>
<td>TT2</td>
<td>9.4386</td>
<td>0.51387</td>
</tr>
<tr>
<td>TT3</td>
<td>510.51</td>
<td>26.389</td>
</tr>
<tr>
<td>MOW</td>
<td>545</td>
<td>28.2</td>
</tr>
</tbody>
</table>
Figure E.1. Anion results from ion chromatography. Chloride and sulfate in mM.
APPENDIX F

pH
What is pH? The answer depends on how one may choose to define it. There are several definitions for what is commonly known as pH and there are significant differences between them. As pH is a central parameter in many geochemical calculations, it is worth defining accurately and completely here.

**Fundamental Definition of pH**

The simplest definition for pH is given below:

\[
pH = -\log [H^+] \quad \text{or} \quad pH = -\log \text{gamma (H}^+\text{)}
\]

or \( pH = -\log \left( \frac{[H^+]}{(\text{mol/kg soln})} \right) \) (DOE, 1994)

**pH Scales**

There are three pH scales in common use (Dickson 1993a, 1993b, Millero, 1996). The three scales are (i) the “free” hydrogen ion concentration scale, (ii) the “total” hydrogen ion scale, and (iii) the “sea water” scale. These scales are explained below. Some of these scales are referred to by multiple names in the literature.

**Free Hydrogen Ion Scale**

\[
pH = -\log [H^+] \quad \text{(Dickson, 1993a)}
\]

**Total Hydrogen Ion Scale or Total Proton Scale (pHT)**

Total Proton Scale (Millero, 1996):

\[
pH_T = -\log [H^+]_T \\
[H^+]_T = [H^+]_F + [\text{HSO}_4^-] \\
T=\text{total} \quad F=\text{free}
\]
or

Total Hydrogen Ion Scale (Dickson, 1993b):

\[ \text{pH}_T = \log m^*(H^+) \quad \text{where} \quad m^*(H^+) = m(H^+) \{1+m^T(SO_4^{2-})/K(HSO_4^-)\} \]

Seawater Scale (pH<sub>SWS</sub>)

\[ [H^+]_{SWS} = [H^+]_F + [HSO_4^-] + [HF] \quad \text{(Millero, 1996)} \]

\[ m(H^+)_{SWS} = m(H^+) \{1+m^T(SO_4^{2-})/K(HSO_4^-) + m^T(F^-)/K(HF)\} \]

Factors Affecting pH

pH is a function of temperature, pressure, and salinity (Millero, 1995). Millero (1995) derived a function for seawater pH as a function of temperature using carbonic acid constants of Roy et al., (1993) (Fig F.1). This function is for fixed S, TA, and TCO₂ and is valid from 0 to 40°C (Millero, 1995).
The temperature compensation function is given by (Millero, 1995):

\[ pH_t = pH_{25} + A + B + C t^2 \] (Valid from 0 to 40°C, S= 30 to 40, pH = 7.5 to 8.5)

Where:

- \( A = -2.6492 - 0.001109 S + 4.9319 \times 10^{-6} S^2 + 5.1872 X - 2.1586 X^2 \)
- \( B = 0.10265 - 0.20322 X + 0.084431 X^2 + 3.1618 \times 10^{-5} S \)
- \( C = 4.4528 \times 10^{-5} \)
- \( X = TA/TCO_2 \)
Practical pH

In addition to the theoretical definitions outlined above, there are specific designations used for certain instruments and/or calibration systems. Sometimes the type of instrument or calibration system used is indicated by the use of a subscript (i.e. $pH_{NBS}$).

Two Buffer Electrode System: $pH_{NBS}$

The $pH$ that is most commonly reported is $pH$ determined with an electrode calibrated with two buffer solutions. In the past this has been infrequently reported (Whitfield, et al., 1985) as $pH$(NBS) or $pH_{NBS}$ indicating that the buffer solutions were traceable to standard solutions from the National Bureau of Standards (NBS). The NBS is now the National Institute of Standards and Technology (NIST).

pH in this Study

All $pH$ measurements in this study are fundamentally the same as $pH_{NBS}$. However, the calibration solutions I used were traceable to the NIST, the successor to the NBS. There has been no use of $pH_{NIST}$ in the literature, and so I have chosen not to use it in this work.
APPENDIX G

SALINITY
Salinity is the primary variable affecting the density of seawater and dilutions of seawater (Millero, 2000b). Salinity is also a very common parameter measured in mixing zone studies. Salinity can be defined in several ways and consequently, caution must be used in how this parameter is measured, reported, and used in calculations. Given its importance, a detailed description of salinity is given here.

**True or Absolute Salinity**

True, Ideal, or Absolute salinity \( S_T \) or \( S_A \) is defined as the grams of inorganic salts in a kilogram of solution (mass fraction)(Millero, 2000b, Fofonoff, 1985). True or absolute salinity is found by complete water analysis or by weighing the residue left upon evaporation. Salinity (True or Absolute) is commonly reported as parts per thousand (ppt), \( \% \), or grams per kilogram. Determining salinity by complete water analysis or by weighing the residue left upon evaporation presents some difficulties. Easier methods, using conductivity, have largely replaced these earlier methods.

**Practical Salinity Scale**

The Practical Salinity Scale of 1978 (PSS 78) is a function that relates salinity to conductivity and temperature (UNESCO, 1981). Salinity values calculated from this function are unitless and are sometimes reported as Practical Salinity Units (PSU). The PSS 78 is only valid from salinity 2 to 42 (UNESCO, 1981). It has been extended below 2 by an additional equation (Hill, et al., 1986).

**Hydrolab MiniSonde Salinity Calculation**

All of the salinity values I report from my study were determined by measuring *in situ* conductivity using the Hydrolab MiniSonde 4. The MiniSonde 4 automatically calculates
salinity by first calculating specific conductance as defined by Miller (1998) and then relating conductance to salinity using the Practical Salinity Scale of 1978.

**Caution in Interpreting Salinity Values**

The wide range of salinity values found in coastal mixing zone aquifers and estuaries creates the potential for significant errors. Compensation functions (used in the base calculations that lead to the final salinity calculation) are often not very accurately defined over such a range. Additional caution must be taken when applying these formulas to determine the salinity of groundwater. Accurately determining the conductivity of groundwater can be complicated by the effects of complexation and protonation of ionic species (Miller, 1998). Complexation and protonation can change the conductivity of the solution and therefore the calculated salinity value.

**PSU or ppt**

In the text of this thesis I refer to salinity in Practical Salinity Units (PSU) and in the appendices A and B salinity is given in parts per thousand (ppt). The graphs in the Appendix A and B were created from data acquired using the MiniSonde 4. The MiniSonde 4 uses a series of functions to convert conductivity to salinity and the final units are ppt. The conversion from ppt to PSU is not simple and for the purposes of gross aquifer characterization the two can be used interchangeably.
APPENDIX H

INSTRUMENT SPECIFICATIONS
### Table H.1 Hydrolab® MiniSonde 4® Instrument Specifications.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>unitless</td>
<td>+/- 0.2</td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>mS/cm</td>
<td>+/- 1% of reading</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>mg/L or % saturation</td>
<td>+/- 0.2mg/L</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>+/- 0.1 °C</td>
</tr>
<tr>
<td>Oxidation-Reduction Potential</td>
<td>mV</td>
<td>+/- 20mV</td>
</tr>
<tr>
<td>Depth</td>
<td>meters</td>
<td>+/- 0.3m</td>
</tr>
</tbody>
</table>
APPENDIX I

YUCATAN TECTONIC STABILITY
Determining the tectonic stability of the Yucatan is not a simple task given the lack of dated materials and difficulty in correlating globally scattered tectonic datums. The presumed “stability” of the Yucatan platform is based on two lines of evidence: (i) there are no obvious geomorphic indications of great subsidence or uplift, and (ii) the elevation of Yucatan deposits from the ~125 ka BP sea level high stand are comparable to the elevations of similarly aged deposits from locations considered to be “stable” (Szabo et al., 1979).

**Radiometric Dating.** The only dates available from suitable Yucatan materials are radiometric dates acquired for beach deposits from 125 ka BP (Szabo et al., 1979) and from a charcoal sample found in a fire pit (Coke and Perry, 1991). These two studies are explained in greater detail below.

**Dated Materials Referenced in this Study**

Szabo et al., (1979) collected corals from five locations on the Yucatan and one from the nearby island of Cozumel. The samples were taken from 2m to 10m above modern sea level. The majority of the samples were taken along the coast between Tulum and Cancun. Szabo et al., (1979) concluded that sea level was 3-6 m above the present level at 120 ka BP to 125 ka BP assuming a tectonically stable coastline.

Coke collected a sample of fire pit charcoal from a site 8.5 km inland (Coke and Perry, 1991). The fire pit site is presently 27.4 m below present day local groundwater table was radiocarbon dated to 8250 (+/- 80) YBP (Coke and Perry, 1991). Unlike the coral dates that indicate where sea level *was* positioned (*i.e.* are constraining indicators), the dating of charcoal indicates where sea level *was not* located (*i.e.* are exclusionary indicators). Coke and Perry (1991) made no correlation between local groundwater table and modern sea level position.
However, the data is still useful as a sea level indicator given the low hydraulic gradient of the region (at the study location the water table is probably less than one meter above sea level).
Mixing Corrosion Defined

In the literature some use *mixing corrosion* to refer to a specific chemical effect and others use the term to refer to a suite of chemical effects. In his landmark 1964 paper, Bogli used *mischungkorrosion* specifically to describe the renewed potential for dissolution produced by mixing calcite-saturated waters each in equilibrium with different $\rho$CO$_2$ (Bogli, 1964). Since the acceptance of this novel paper this type of mixing effect has been often referred to as ‘Bogli Mixing Corrosion’ or simply ‘Mixing Corrosion’. Wigley and Plummer (1976) objected to this specific use of the term because, as they noted, other mixing processes (not just $\Delta$pCO$_2$) can also produce corrosive mixtures from saturated end-members.

Given the ambiguity of meaning for *mixing corrosion* I considered abandoning the term altogether and proposing a new, clearly defined term. However, in the interest of simplicity, I will clarify the term and continue using it. In this paper, Mixing Corrosion is defined as:

The dissolution of minerals resulting from the sum of all chemical effects that take place when heterogeneous waters mix.

These chemical effects include, but may not be limited to: $\Delta$pCO$_2$, temperature effects, the ionic strength effect, complexing, and the common ion effect.
**Terminology Defined**

To accurately define the features in density stratified aquifers, I have borrowed and modified terminology more traditionally applied to oceanography and limnology.

Pycnocline: A zone having a marked change in water density as a function of water depth. This density difference may be due to temperature differences (thermocline) or salinity (halocline).

Thermocline: A sharp, vertical temperature gradient that marks a contact zone between water masses having significantly different temperatures.

Chemocline: A zone having a marked change in chemistry as a function of water depth. An example of a chemocline could be the anoxic/oxic boundary (or related hydrogen sulfide layer).

Halocline: A zone in the water column with a sharp change in salinity as a function of water depth.

Primary Halocline: The density interface between saline groundwater with salinity equal to or greater than the adjacent ocean and overlying flows of lower salinity.

Endmember: A designated, type solution used in geochemical reaction modeling.
Note that the spelling of endmember is variously given as “end-member”, “end member” and “endmember” in the literature.
APPENDIX L

MIXING RATIO CHART
Fig L.1. Salinity Mixing Model for TRA. This model assumes mixing between two endmembers with salinities of 1 and 35.

Figure L.1. is a guide for assessing the extent of mixing between saline groundwater and the interior freshwater unit. Sample Salinity is the salinity of the mixed solution produced by mixing two end-member solutions: a freshwater member with salinity of one and a saline member (saline groundwater or seawater) with salinity of 35. Plotted from Equation L.1

\[ \left( \frac{S_{\text{mix}} - S_{\text{fresh}}}{S_{\text{saline}} - S_{\text{fresh}}} \right) \times 100 = \text{mixing (by mass) percentage} \]

\( S_{\text{mix}} = \) salinity of mixed sample

\( S_{\text{fresh}} = \) salinity of interior freshwater lens (set at 1)

\( S_{\text{saline}} = \) salinity of saline groundwater (set at 35)
Density and Equation of State

Water density is primarily a function of temperature and salinity (Millero and Poisson, 1981; Fofonoff, 1985). Functions, or equations of state, have been created for a range of environmental waters (Millero and Poisson, 1981; Millero, 1974; Millero 2000; Fofonoff, 1985).

Equation of State for TRA

Given the large range in salinity found in the TRA, some care must be taken when selecting an appropriate equation of state. Millero (1974) adapted an early version of the equation of state for seawater for use with intermediate salinity estuarine waters. Millero (2000) defined an equation of state for lakes (salinity less than 1). Together, Millero’s three papers conveniently provide an adaptable equation of state that works well across the full range of salinities found in the mixing zones of the TRA (Figure M.1.).
Fig M.1. Equation of state relating density to salinity and temperature. Graph produced from equation of state as given by Millero (2000). Salinity line is for constant temperature of 25°C. Temperature line is for constant salinity of 35 PSU.
Figure M.2. Change in density with change in salinity and temperature. Note that the change in density as a function of temperature is much less than the change in density as a function of salinity. Equation of state from Millero (2000).
REFERENCES


Dickson, A.G., 1993b, pH buffers for sea water media based on the total hydrogen ion concentration scale, *Deep-Sea Research*, v.1, n.1, p.107-118


Dreybrodt, W., 1981, Mixing corrosion in CaCO3-CO2-H2O systems and its role in the karstification of limestone areas, *Chemical Geology* v. 32, p. 221.


Kris Esterson was born April 22, 1974. He earned a BS in Geology from the University of Alaska Fairbanks in 1997. He is an active caver and cave diver.