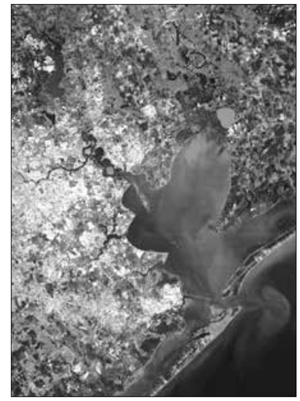
# Experiment 9



# Precipitation Titrations

## *Determining the Salinity of a Bay Water Sample*

**In this experiment, the salinity profile of the water in the San Antonio Bay is modeled based on samples collected in March, a wet month, and in April. The salinity is calculated from an experimentally determined chloride ion concentration. Precipitation titrations, using silver nitrate as the titrant, are performed to analyze the chloride ion concentration.**

**Learning Objectives:** Students will learn to

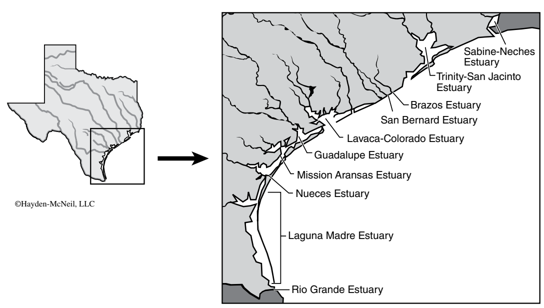
- Calculate the salinity of a salt water sample in ppt
- Analyze a complex data set
- Perform cooperative research work in a team environment

**Experimental Objectives:** Students will gain experience in the following experimental techniques

- Dilution of concentrated solutions
- The handling of light-sensitive silver nitrate solutions
- Precipitation titrations
- Endpoint determination using an adsorption indicator

## Introduction

### Context: Salinity in the San Antonio Bay




The 367-mile stretch of the Texas coastline impacts the aspects of Texans' lives in areas extending from sports and recreation to commercial enterprises. The coastline represents a treasure that contributes approximately $3 billion to the state economy. The coastal area is made up of 1.5 million acres of open bays, 1.1 million acres of wetlands, and about 250,000 acres of submerged aquatic vegetation. The Texas coastal region is home to over 400 species of native and migratory birds and untold numbers of crustaceans and fish. Factors such as temperature, pH, salinity, and turbidity are important in determining the biological health of the ecosystem. Changes in salinity in the San Antonio Bay, which is fed by the Guadalupe River, are the focus of this experiment.

## Chemical Principles: Salinity

**Salinity** is defined as the amount of salt dissolved in a sample of water. Salinity is typically reported in grams salt per liter sample or **parts per thousand** (ppt). The most abundant dissolved salt in seawater is sodium chloride, NaCl. The salinity of a salt water sample can therefore be calculated as the ppt NaCl concentration.

$$\frac{\text{g NaCl}}{\text{g salt water}} \times 1000$$

The weight of NaCl in a saline solution can be calculated if the chloride ion concentration in molarity, $[Cl^-]$, is known. The equation above can be rewritten in terms of $[Cl^-]$ ($FW_{NaCl}$ = formula weight of NaCl).

$$\frac{[Cl^-]V_{\text{salt water sample}}FW_{NaCl}}{\text{g salt water}} \times 1000$$

On average the salinity of oceanic waters is 35 ppt. Rivers have a much lower average salinity of 1.6 ppt. The salinity profiles of bays and estuaries where fresh and saltwater sources meet show a large variance in salinity according to geographic location, time of day and time of year.

## Analytical Technique: Precipitation Titrations

In this experiment, the chloride ion concentration in bay water samples will be determined through titration with standardized solutions of silver nitrate, $AgNO_3$. The **solubility rules** tell us that silver ions ($Ag^+$) will form an insoluble solid when reacted with chloride ions ($Cl^-$). The net ionic reaction below represents the formation of a white silver chloride precipitate.

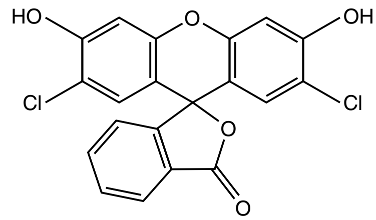
$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

Before the equivalence point there is an excess of the chloride ion in solution. As the silver ions are added, the chloride ion concentration slowly decreases and the amount of precipitate, silver chloride, increases. At the equivalence point, all of the chloride ions in solution have reacted and no more precipitate will form. After the equivalence point, the excess silver ion concentration increases and is in excess.

Titrations using silver nitrate, also known as **argentometric titrations**, are therefore **precipitation titrations**. Argentometric methods are also used in the determination of other halides, thiocyanate, cyanide, mercaptans, inorganic anions, and fatty acids.

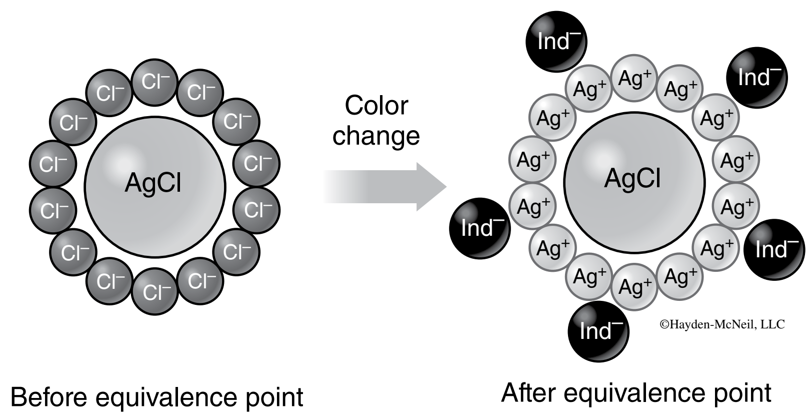
The equivalence point of a precipitation titration is defined as being the point at which the precipitate no longer forms. Visual determination of the endpoint of a precipitation titration can, however, be tricky. A series of methods based upon the use of **chemical indicators**, brightly colored adsorbent species or precipitates, have been developed to aid in endpoint determination.

**Fajan's method**, used to determine chloride ion concentration in this experiment, relies on the use of an adsorption indicator, dichlorofluorescein. The structure of dichlorofluorescein, a weak organic acid, is shown below.



dichlorofluorescein

Adsorption indicators form a colored layer as they adsorb to the surface of particles in solution. The silver chloride particles that form before the equivalence point in an argentometric titration will preferentially adsorb the excess chloride ions over any indicator anions. The negative charge surrounding the silver chloride particles prevents the adsorption of the dichlorofluoresceinate anions ($Ind^-$). However, once the equivalence point is reached all chloride anions ($Cl^-$) have reacted and silver cations ($Ag^+$) begin to adsorb on the surface of the precipitate. Attracted by the positive charge of the silver cations, the dichlorofluoresceinate anions then form a pink layer as they adsorb to the surface of the silver chloride precipitate (see following figure). The color change associated with the formation of the pink layer signals the endpoint of the titration.




The light-sensitive nature of silver nitrate solutions and the difficulty associated with recognizing the endpoint of a precipitation reaction can make argentometric determinations challenging. Provided that the proper precautions are taken, argentometric methods can be successfully implemented. Silver cations are reduced to silver metal in bright light. Therefore silver solutions are typically stored in dark colored containers and titrations are performed in low light. Silver solutions containing a fine gray precipitate, reduced silver, should not be used. The endpoints of precipitation titrations are not often sharp. Increasing the precipitate surface area promotes more adsorption of the indicator and results in sharper endpoints. The addition of the carbohydrate dextrin to the analyte solution prevents the silver chloride particles from coagulating thereby increasing the surface area of the precipitate. This in turn provides more pink color due to a higher degree of association between the silver cations and dichlorofluoresceinate anions.

## Focus

Lab classes will determine the salinity of samples collected throughout the San Antonio Bay. The bay water samples were collected in March, a month with a high average rainfall, and April. Samples were collected from 12 different geographic locations in the bay. Each pair of lab partners is responsible for determining the salinity at one particular location (2 samples). Once the salinity at all twelve locations (24 samples) has been determined, students prepare salinity profiles of the entire bay for each month. Conclusions are then drawn about the direction of the movement of water through the bay to the Gulf of Mexico.

## Experiment

In this experiment the chloride ion concentration of two bay water samples from the same geographic location in the San Antonio Bay will be determined via precipitation titration using silver nitrate as the titrant. An initial series of practice titrations of a standardized sodium chloride solution, using dichlorofluorescein as an indicator, aids in endpoint recognition.

### Health, Safety, and Environmental (HS&E) Items

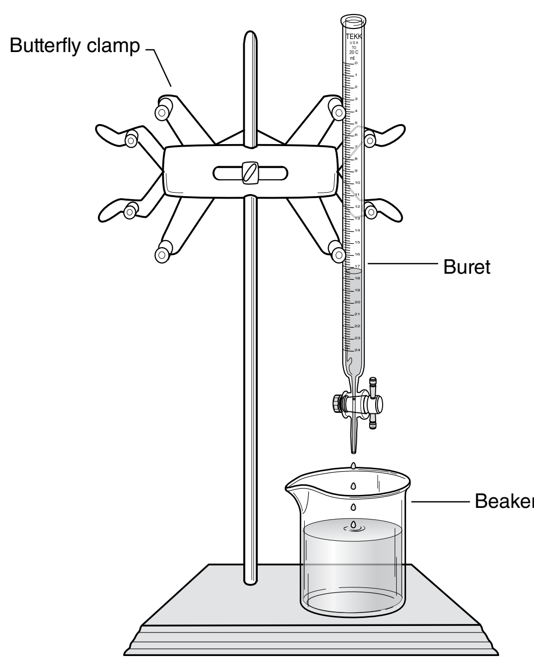
You will be working with dilute solutions of silver nitrate, dichlorofluorescein indicator, dextrin, and sodium chloride solutions. Use appropriate personal protection equipment where necessary to protect yourself. Wear appropriate eye protection (goggles) at all times. Wash your hands with running water for 15 minutes if your skin comes in contact with any of the solutions during today's experiment. All waste containing silver will be collected in waste jars. Silver nitrate will stain clothes, skin, and jewelry.

### Chemicals

0.040 M standard NaCl solution
0.010 M standard $AgNO_3$
bay water samples
dextrin
dichlorofluorescein indicator solution
distilled water

### Equipment

600 mL beaker
25 mL graduated cylinder
10 mL graduated cylinder
3 50 mL beakers
10 mL volumetric flask
fast release pump
spatula
2 mL serological pipet
butterfly clamp
ring stand
buret
10 mL serological pipet
buret funnel



## Experimental Procedure

### *Part A: Titration of Standard 0.040 M NaCl Solution with Standard 0.010 M $AgNO_3$*

Recognizing the endpoint of a precipitation titration requires practice with the chosen indicator. Solutions of known concentration (predetermined equivalence points) are therefore commonly titrated prior to performing the determination of any unknown samples.

1. Acquire a 600 mL beaker for waste collection, a 25 mL graduated cylinder for the silver nitrate solution, and a 10 mL graduated cylinder for the NaCl solution. Fill a water bottle with distilled water. *Do not use tap water* for this experiment.

2. In a 10 mL graduated cylinder obtain 5 mL of 0.040 M NaCl solution. Rinse a 2 mL serological pipet with a small amount (~1 mL) of the NaCl solution. Pipet 1.0 mL of the NaCl solution into a 50 mL beaker. Add approximately 9 mL of distilled water to the sample by filling the beaker to the 10 mL mark.

3. Obtain 15 mL of standardized 0.0100 M $AgNO_3$ in a 25 mL graduated cylinder. Attach a butterfly clamp to a ring stand and place a buret into the butterfly clamp. Make sure that the buret stopcock is closed. Rinse the buret with a small amount (~1 mL) of $AgNO_3$ catching all waste in the 600 mL waste beaker. Pour the remaining 14 mL of $AgNO_3$ into the buret.

4. Calculate the amount of 0.010 M $AgNO_3$ required to titrate the 1 mL sample of 0.040 M NaCl.

$$V_{AgNO_3}M_{AgNO_3} = V_{NaCl}M_{NaCl}$$

5. When using Fajan's method the endpoint is more clearly seen when the indicator is added close to the endpoint. Record the initial volume of $AgNO_3$ in the buret. Titrate to within 0.5 mL of the anticipated endpoint. Add 2 drops of dichlorofluorescein indicator solution and just enough dextrin to cover the end of the tip of a spatula.

6. Continue to titrate the sample while vigorously swirling the beaker. The transition from an orange/tan colored solution to a milky pink suspension signals the endpoint of the titration.

7. Note the final volume of the buret. Determine the volume of $AgNO_3$ used to reach the endpoint of the titration. This volume should be within 0.1 mL of the calculated equivalence point.

8. Pour all waste into the 600 mL waste beaker. Rinse the three 50 mL beakers with distilled water. Collect all rinse water in the 600 mL waste beaker.

### *Part B: Titration of Bay Water Samples*

1. Obtain bay water samples collected in March and April for one geographic location. The latitude and longitude for your pair of samples **must** match. Record the geographic location in your lab notebook.

2. Rinse a 2 mL serological pipet with a small amount (~1 mL) of the March bay water sample. Pipet 1.0 mL of the March sample into each of three clean 50 mL beakers. Add approximately 19 mL of distilled water to each sample by filling the beakers to the 20 mL mark.

3. Refill the buret with an additional 10 mL of 0.010 M $AgNO_3$ solution.

4. Add 2 drops of dichlorofluorescein indicator solution and just enough dextrin to cover the end of the tip of a spatula to one of the three beakers. An initial fast titration will be performed with this sample to determine the approximate endpoint.

5. Record the initial volume of $AgNO_3$ in the buret. Adjust the flow from the buret to a steady stream of drops while vigorously swirling the beaker below. Watching the color of the solution carefully estimate the volume at which the endpoint is reached. Record the estimated endpoint volume from the buret and calculate the volume of $AgNO_3$ required to reach the titration endpoint. If you add more than 10 mL of the $AgNO_3$ solution and have not reached your endpoint, then you will need to dilute your sample, as described in step 6. Otherwise, proceed to step 7.

6. Pipet 1.0 mL of the March sample into a 10 mL volumetric flask. Fill the flask to the 10 mL mark with distilled water and gently mix the solution. Make a note of this dilution in your lab notebook. Prepare three new March samples to titrate (discard your samples prepared in step 2) by pipetting 1.0 mL of the diluted solution into each of three clean 50 mL beakers. Add approximately 19 mL of distilled water to each sample by filling the beakers to the 20 mL mark. Add 10 more mL of $AgNO_3$ to the buret. Repeat the fast titration (steps 4 and 5) and estimate the titration endpoint.

7. Making sure that there is enough $AgNO_3$ in the buret to complete the titration, titrate one of the remaining two March samples to within 0.5 mL of the endpoint. Add 2 drops of dichlorofluorescein indicator solution and just enough dextrin to cover the end of the tip of a spatula. Continue adding $AgNO_3$ dropwise until the endpoint is reached. Record the final volume on the buret. Repeat this step for the final March sample. Subsequent titrations may be necessary if the endpoint volumes do not agree to within 0.2 mL.

8. Pour all waste into the 600 mL waste beaker. Rinse the three 50 mL beakers with distilled water. Collect all rinse water in the 600 mL waste beaker.

9. Repeat steps 2–8 for the April bay water sample.

10. Pour all waste into the labeled waste containers.

11. Clean all glassware and return it to the appropriate bins in the back of the lab. Wipe down the benchtop at your work station with a damp paper towel before leaving lab.

## Post Lab Exercises

All data reduction will be completed in class. Before leaving class collect the class data including the salinity of all 12 geographic locations in March and April.

### Data Reduction and Analysis

Complete the worksheet following this lab.

# Data Reduction and Analysis

# Experiment 9

## Precipitation Titrations

*Determining the Salinity of a Bay Water Sample*

**Name** ______________________ **Lab Partner** ______________________

**Section** __________ **TA Name** ______________________ **Score** __________

The following should be attached to this worksheet:

❑ Notebook copy.

**Data Summary**

Geographic location ______________________________

Volume of $AgNO_3$ to titrate bay water samples

| Sample | Fast Titration | Trial 1 | Trial 2 | Average (Trials 1 & 2) |
|---|---|---|---|---|
| March | | | | |
| April | | | | |

Were either of your samples diluted? If so, identify them. ______________________________

Write the fully balanced and net ionic equations associated with the titration of a sample containing sodium chloride with silver nitrate.

Fully Balanced Equation:

Net Ionic Equation:

**Calculation of the salinity of the San Antonio Bay samples.**

a. Calculate the number of moles of $AgNO_3$ required to titrate each of the bay water samples. Use the average volume of $AgNO_3$.

| **General Equation:** | |
|---|---|
| March Sample | April Sample |

March average moles $AgNO_3$ ___________________

April average moles $AgNO_3$ ___________________

b. Using the balanced equations on page 147, calculate the average number of moles of NaCl in each of the titrated samples. Remember to account for any dilutions you performed on your samples.

| **General Equation:** | |
|---|---|
| March Sample | April Sample |

March average moles NaCl ___________________

April average moles NaCl ___________________

c. Calculate the average number of grams of NaCl in each of the titrated samples.

| **General Equation:** | |
|---|---|
| March Sample | April Sample |

March average grams NaCl ___________________

April average grams NaCl ___________________

## Data Reduction and Analysis

# Experiment 9

### Precipitation Titrations

*Determining the Salinity of a Bay Water Sample*

**Name** **Lab Partner**

**Section** **TA Name** **Score**

d. Using the balanced equations on page 147, calculate the salinity in ppt of each of the samples. It can be assumed that the density of the bay water is 1 g/mL. *Hint: The volume of bay water titrated will depend on the dilution factor. How many mL of bay water are titrated in a diluted sample? How many mL of bay water are titrated in an undiluted sample?*

$$\text{Salinity (ppt)} = \frac{\text{g NaCl}}{\text{g bay water}} \times 1000$$

| **General Equation:** | |
|---|---|
| March Sample | April Sample |

March average salinity ________________

April average salinity __________________

Report the salinity data for your lab section in the table below.

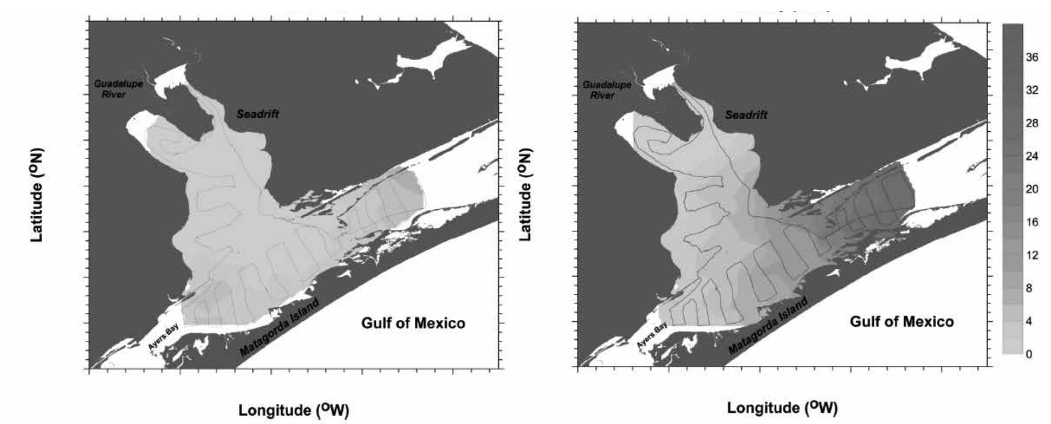
**Class Salinity Data (ppt)**

| Geographic Location | March | April |
|---|---|---|
| 28°42' × 96°77' | | |
| 28°40' × 96°80' | | |
| 28°38' × 96°78' | | |
| 28°35' × 96°75' | | |
| 28°32' × 96°76' | | |
| 28°25' × 96°72' | | |
| 28°20' × 96°80' | | |
| 28°32' × 96°71' | | |
| 28°32' × 96°60' | | |
| 28°32' × 96°52' | | |
| 28°28' × 96°76' | | |
| 28°28' × 96°68' | | |

Find each geographic location on the maps provided on the following pages. Indicate the salinity determined at each location on the map. One map represents the March data while the other represents the April data.

The average rainfall in March is typically higher than that of April. Do your results reflect the difference in rainfall? Explain your answer.

Compare your map of salinity with the real data collected by Dr. Stephen Davis in the Department of Wildlife and Fisheries Sciences, shown below, at Texas A&M. The plot on the left is a plot of the salinity for San Antonio Bay, which is fed by the Guadalupe River, in March, a rainy month. The plot on the right is of the salinity for San Antonio Bay in April. The scale on the far right indicates the concentration of salinity in Practical Salinity Units (PSU). Practical salinity is determined by measuring the conductivity of water samples. The conductivity is directly related to salt (electrolyte) concentration. Ayers Bay connects the Gulf of Mexico to San Antonio Bay at the bottom left of each plot. Based on the above information, answer the following questions:

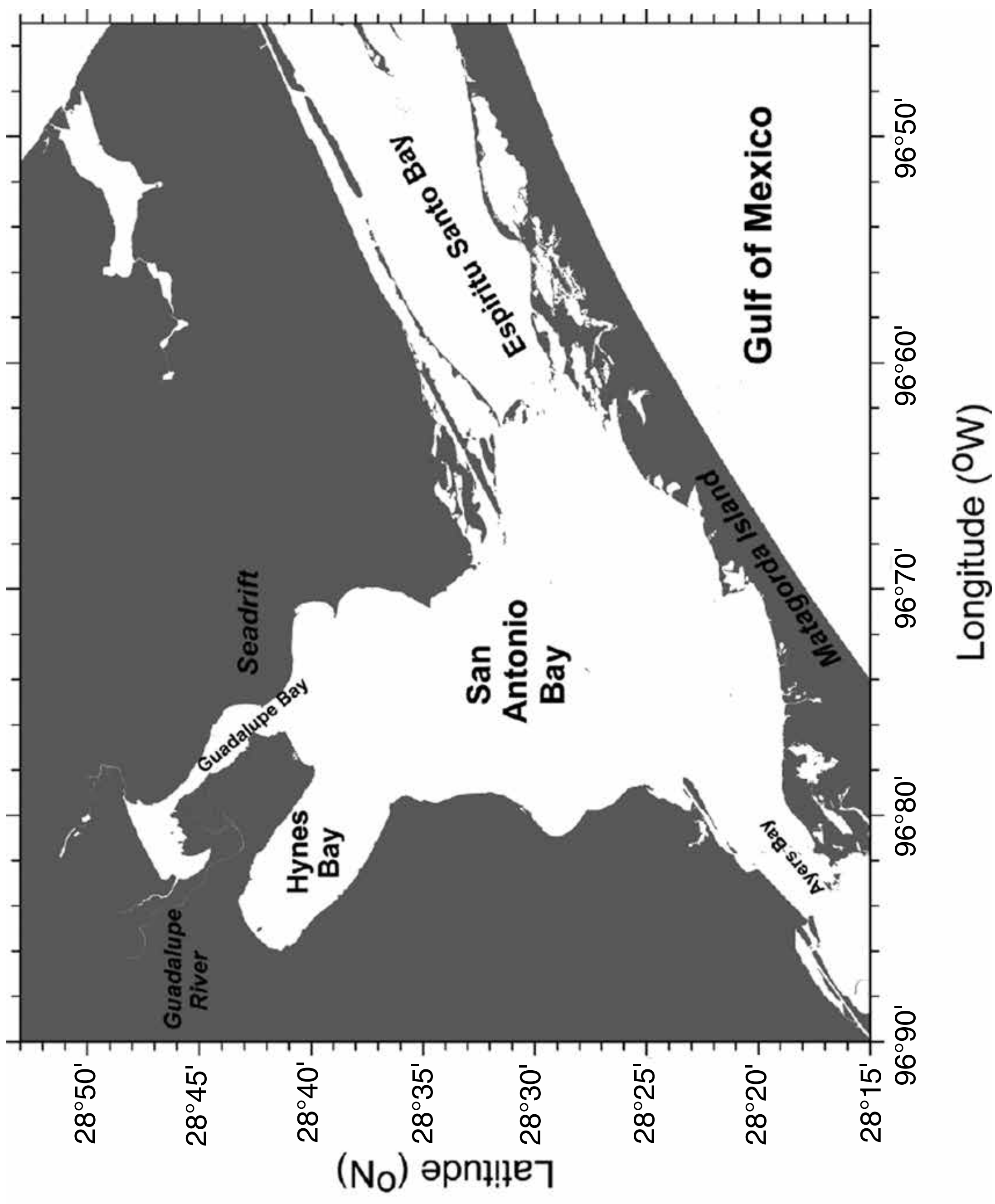



*March Salinity Data* *April Salinity Data*

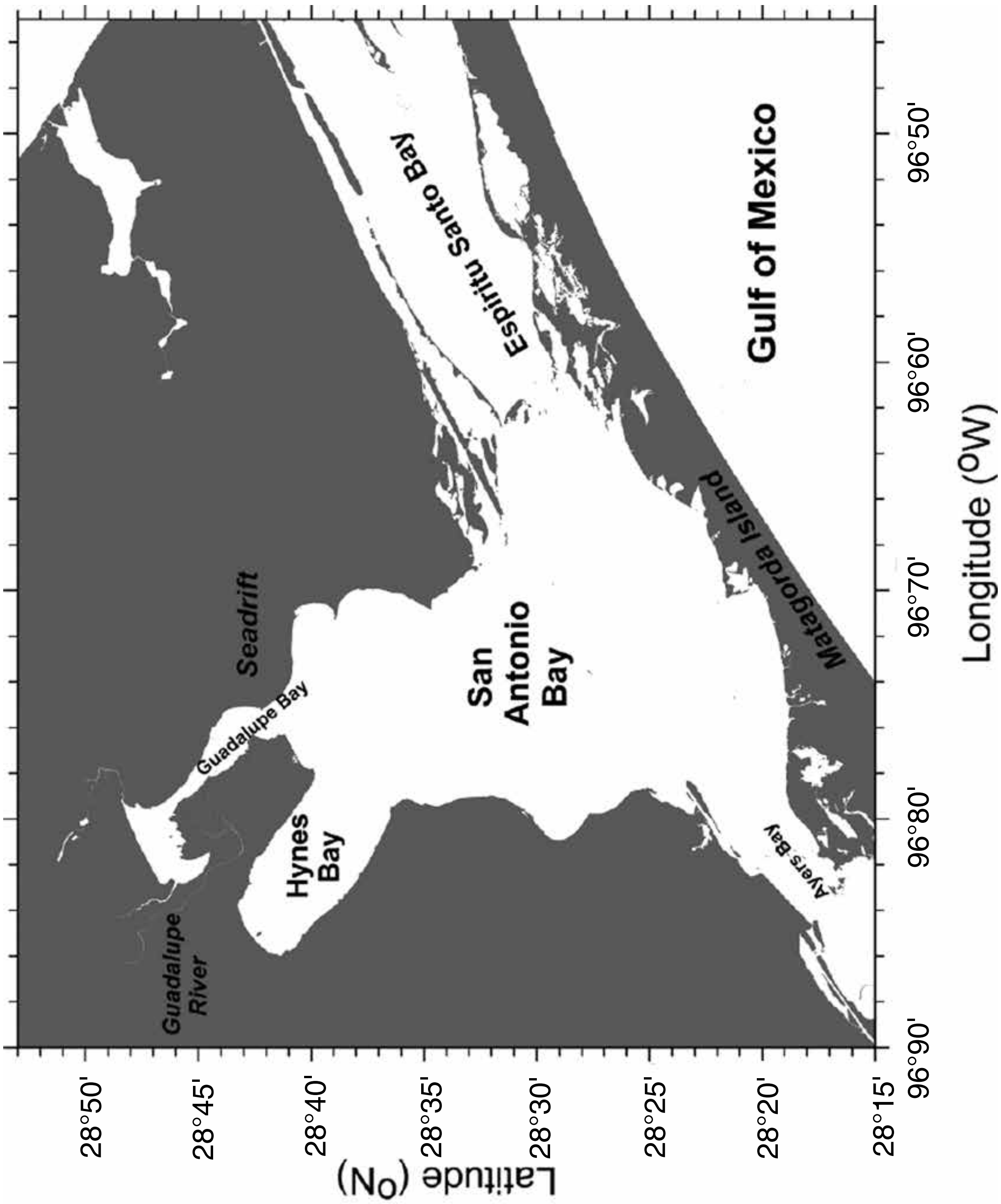
1. How do the March and April maps of Dr. Davis's data differ?

2. Does the data obtained by your class reflect the same trend?

3. What conclusions can you draw about the direction of water movement between the bay and Gulf of Mexico through Ayers Bay?




**March Salinity Data (PSU)**




**April Salinity Data (PSU)**