Ocean Acidification: CO_2 in the Ocean

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Equipment needed for each student group:

- 1 400 mL "Rinse" beaker
- 1 150 mL "Buffer Titration" beaker
- 1 250 mL plastic Erlenmeyer flask
- 1 50 mL "0.02N HCl" beaker
- 1 100 mL graduated cylinder
- 1 calibrated pH meter
- 1 10 mL pipet with filler
- 1 DI squirt bottle
- 1 stir stick
- 1 dropper
- 1 piece of coral
- Dissecting Scope
- funnel

For general class use:

- Seawater
- Deionized (DI) water
- Bromothymol Blue (BTB)
- 0.02N HCl
- 0.5N HCl
- Straws
- Powdered chalk ($MgCO_3$)
- Balance
- Sandpaper

DISCUSSION: *CO_2 in the Ocean*

The oceans currently behave as carbon sinks because they absorb approximately 25-30% of the carbon dioxide (CO_2) put into the atmosphere by human activities such as fossil fuel burning (Figure 1).

As the oceans continue to absorb ever-increasing amounts of atmospheric CO_2, the chemistry of the ocean changes according to the following reactions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

CO_2 dissolves into seawater and reacts with water molecules to form carbonic acid. The ultimate result of these chemical reactions is an increase in CO_2 and a decrease in carbonate (CO_3^{2-}) and pH of seawater (Figure 2). The decrease in pH (i.e., increase in acidity) has negative consequences for marine organisms, marine food webs and entire ecosystems. In fact, many organisms, including ourselves, cannot tolerate changes in pH. For example, human blood has a narrow pH range of 7.35 - 7.45. If our blood pH were to change even slightly, our health could be negatively impacted. Marine organisms are no different.

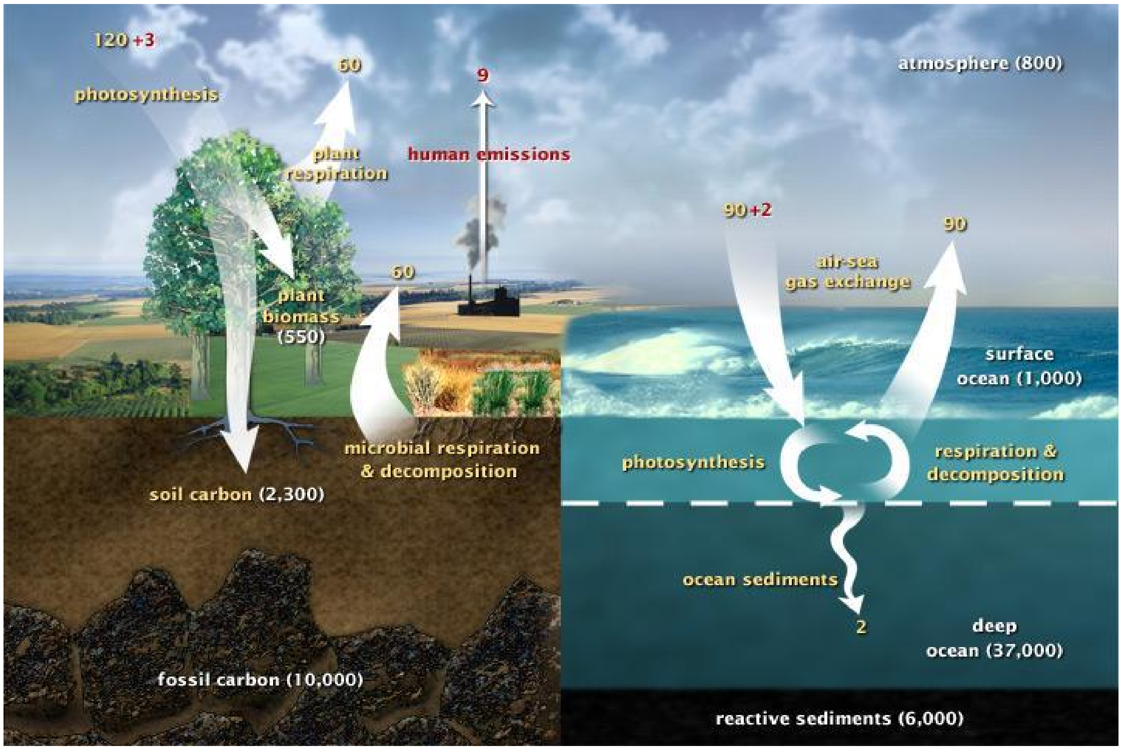

Figure 1. This diagram of the fast carbon cycle shows the movement of carbon between land, atmosphere, and oceans. Yellow numbers are natural fluxes, and red are human contributions in gigatons of carbon per year. White numbers indicate stored carbon. (Diagram adapted from U.S. DOE, Biological and Environmental Research Information System.)

Ocean acidity, as measured by pH, has increased by 30% since the Industrial Revolution, and scientists predict pH will continue to change as increasing amounts of carbon dioxide are absorbed by the world's oceans (Fig 2). Because the chemistry of the oceans is important to life, subtle changes in that chemistry may have significant effects on the health of individual species and on entire ecosystems. Corals and other shell-builders such as oysters, lobsters and pteropods may be at risk as ocean pH becomes more acidic.

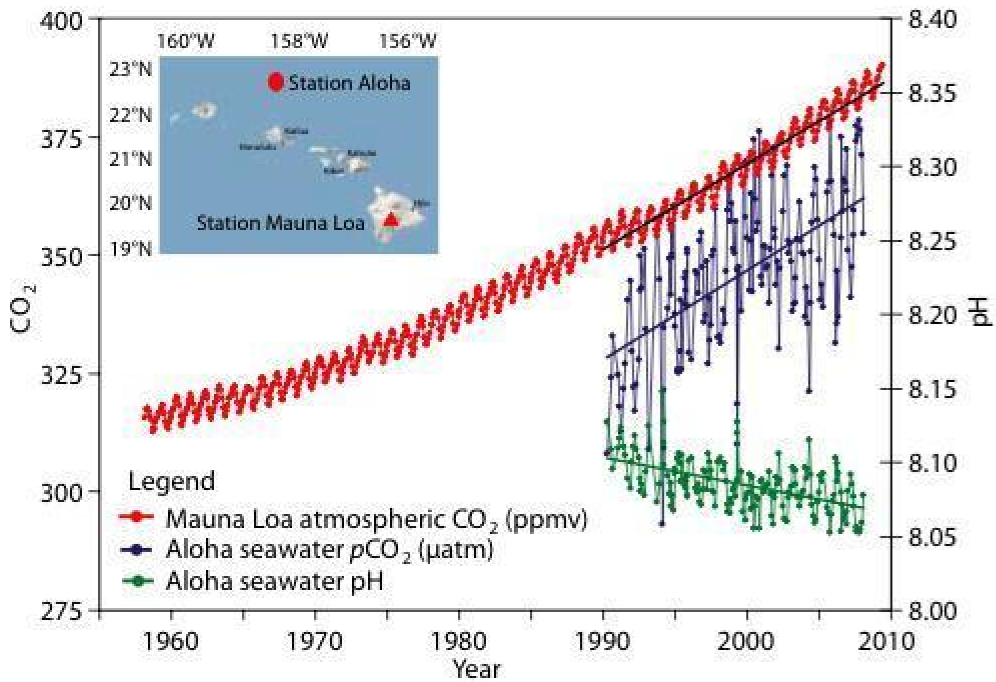

Figure 2. The Keeling Curve atmospheric CO_2 from Mauna Loa (—); Pacific Ocean CO_2 (—) and pH (—). Source: Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL; HOTS/Aloha data: Dr. David Karl, University of Hawaii. Graph from Earthlabs.

Note that each data set shows considerable variability in yearly measurements but when this variability is averaged over time, definite trends can be observed.

DISCUSSION: *Calcium Carbonate Shells*

Many marine organisms make shells by extracting calcium (Ca^{2+}) and carbonate (CO_3^{2-}) from surrounding seawater and making calcium carbonate ($CaCO_3$) shells according to the reaction:

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_{3(solid)}$$

These organisms include corals, mussels, clams, oysters and even microscopic organisms like Coccolithophorids (a phytoplankton) and Foraminifera (a zooplankton). Hence, as the oceans absorb more CO_2, and the CO_3^{2-} concentration declines, calcifying organisms will find it harder and harder to form their $CaCO_3$ shells and skeletons. Eventually, these structures will begin to dissolve.

EXERCISE 1: *Determining a causal relationship between CO_2 and pH: Does a change in CO_2 cause a change in pH?*

For this experiment, you will use a chemical called bromothymol blue (BTB). This chemical is commonly used in many laboratory experiments to test for a change in pH. You will add CO_2 to plain tap water. The source of CO_2 you will use in this experiment will be the CO_2 that you exhale.

1. Pour 50 ml of BTB solution into the plastic Erlenmeyer flask. Make note of its color on your form.
2. Exhale your CO_2 through the straw into the flask. Make sure you don't "suck up" any of the BTB

solution into your straw and mouth.

3. When a color change has occurred, stop exhaling CO_2 into the straw. Compare your color change to Figure 3.

Figure 3. Bromothymol Blue pH indicator dye in an acidic, neutral, and basic (alkaline) solution - left to right.

Answer the following questions:

A. What happened to the bromothymol blue (BTB) solution when you added carbon dioxide (CO_2)?

B. Based on what you observed in the experiment, how do you think increasing carbon dioxide levels affects the ocean?

DISCUSSION: *Seawater – a natural buffer system*

One of the remarkable capabilities of seawater is its ability to act as a buffer. A buffer has special chemical properties that prevent large dramatic fluctuations in the pH of a solution to occur. The term pH is related to the concentration of hydrogen ions, commonly denoted as $[H^+]$, that are present in a solution, where pH = -log $[H^+]$. The pH scale ranges from 0 to 14 with 7 being neutral, solutions less than 7 being acidic and solutions greater than 7 being alkaline (or basic) (Figure 4). As the hydrogen ion concentration $[H^+]$ increases, the pH decreases, and a solution becomes more acidic. If the hydrogen ion concentration decreases, the pH increases, making a solution more basic. The strength of a buffering compound is its ability to receive hydrogen ions if they are available in excess or donate hydrogen ions if they are scarce.

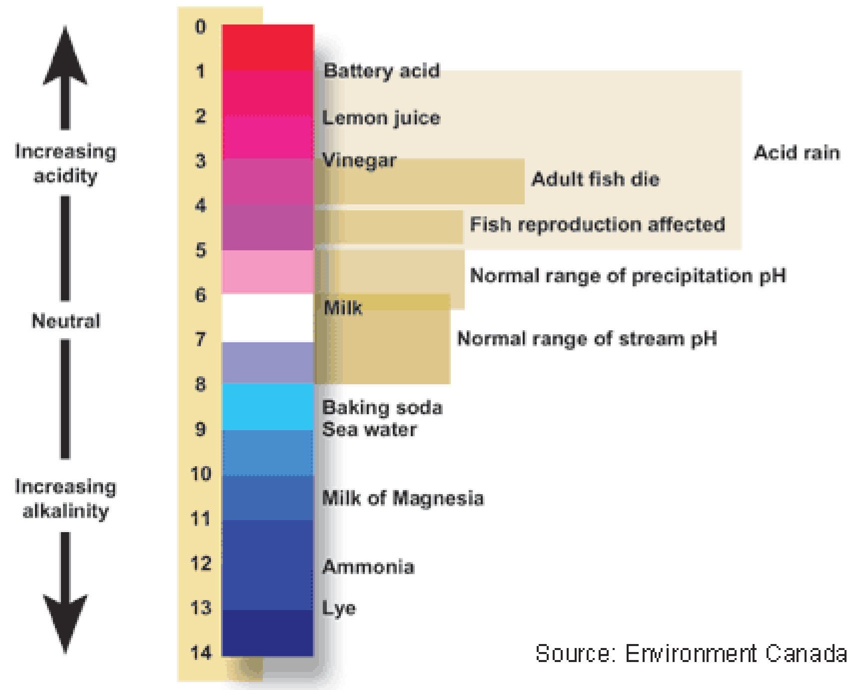

Figure 4. pH diagram showing the pH of some common solutions.

The ocean's buffering capacity allows a relatively stable environment for many sensitive organisms to thrive. However, as seen in the previous discussion, more and more carbon dioxide is being introduced into the atmosphere and, subsequently, being absorbed by the surface ocean. The basic chemistry equations of seawater's buffering system are:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$
$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^-$$

Note that addition of more carbon dioxide results in more hydrogen atoms (H^+) which increases the acidity and lowers the pH. Because of the buffering chemistry of seawater, the pH of the surface ocean has shown little change in recent years. We will examine the strength of this natural buffering system using two water samples; water and seawater. We will observe the consequences of when a sample's buffering capacity is surpassed by adding $CaCO_3$.

EXERCISE 2: *Assessing the buffer capacity of seawater*

1. Using the graduated cylinder, measure out 100mL of the freshwater (DI) and pour it in the sample beaker.
2. Using beaker labeled 0.02N HCl (not the sample beaker), measure out about 20 mL of 0.02N HCl. Do not use this until step 6.
3. Using squirt bottle, rinse the pH electrode off, catching the "spray" in the beaker labeled 'Rinse Water'.

4. Carefully lower the electrode into the sample (DI water) solution so that the bulb is covered with solution. Do NOT rest the electrode on the bottom of the beaker.
5. Wait until the pH has stabilized, and record the pH. (Note: if the pH is bouncing between two numbers, wait just one minute, choose one and move on.). Record the pH in **Table 1**.
6. Using the pipette, add 1mL of 0.02N HCl.
7. Stir with the stir stick.
8. Again take a pH measurement when the pH has stabilized. Record the value in Table 1.
9. Repeat until a total of 10mL of acid has been added. Record each pH value in Table 1.
10. Rinse the electrode off, again catching the rinse water and repeat the process for a Seawater sample. Record the pH values for this sample in **Table 2**.
11. Next add 0.25g $CaCO_3$ (the powdered chalk available near the scale) to the seawater sample, and stir for 5 minutes.
12. Measure the pH. Record values for this modified sample in **Table 3**.
13. Repeat until a total of another 5 mL of acid has been added. Record the value in Table 3
14. Rinse the electrode with DI water using the squirt bottle and place back into the storage solution.
15. Using all of your collected data, plot your results in Figure 5 an x-y scatter graph with pH on the y-axis and acid volume added on the x-axis.

TABLE 1. pH for the freshwater (DI) sample.

Volume of Acid Added (mL)	pH
0	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

TABLE 2. pH for the seawater sample.

Volume of Acid Added (mL)	pH
0	
1	
2	
3	

4	
5	
6	
7	
8	
9	
10	

TABLE 3. pH for the seawater sample with added $CaCO_3$.

Volume of Acid Added (mL)	pH
0 *(pH after adding $CaCO_3$)*	
1	
2	
3	
4	
5	

Draw the curves for each trial in Figure 6. Use a (o) for the Freshwater, a (x) for Seawater, and a (*) for the Seawater after $CaCO_3$ added.

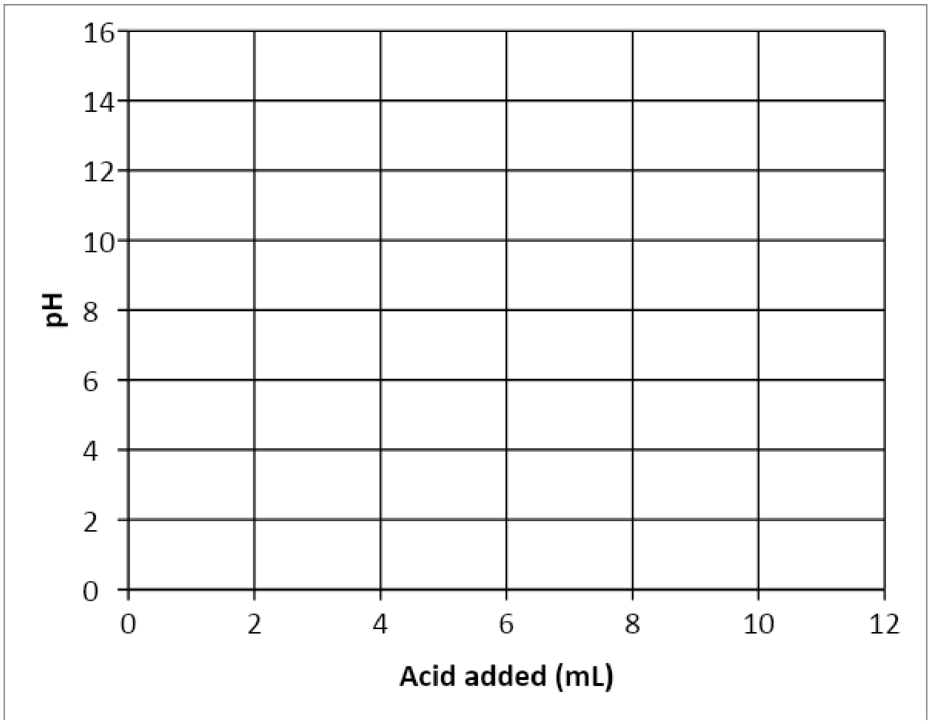

Figure 5. pH versus acid added for the 3 water samples.

Answer the following questions:

A. Which solution had the overall greater pH change?

B. Which solution had a faster rate of change?

C. How did the seawater trials compare to the freshwater trials?

EXERCISE 3: *The effects of acid on biology in the ocean*

To examine the consequences of acidification of the oceans, we will add acid to a piece of $CaCO_3$ (from an old dead coral sample).

$$H^+ + CaCO_3 \quad Ca^{2+} + HCO_3^-$$

1. Observe the surface under a microscope and describe the condition.
2. Add a few drops of 0.5N HCl using the dropper.
3. Again observe under the microscope.

Answer the following questions:

A. What happened when you added the acid?

B. Describe the difference in the coral before and after the addition of the acid.

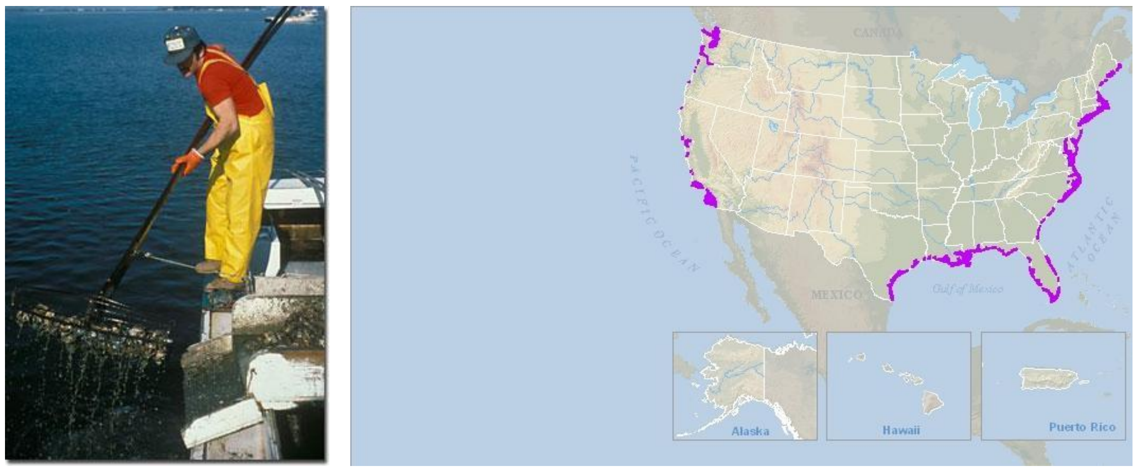

Figure 6. Oyster harvesting (left) and locations marked in purple of U.S. oyster beds (right). Photos from (http://laterallineco.com/blog/chesapeake-bay-oyster-advisory-commission-recommends-comprehensive-approach-to-oyster-restoration-in-maryland/ and http://chesapeakebay.noaa.gov/oysters/oyster-reefs)

C. Oysters make $CaCO_3$ shells. Oysters are a substantial commercial fishery. Considering this experiment, what might happen to Oyster Beds due to the recent increases in carbon dioxide in the atmosphere? EXPLAIN.

Discussion: The Flower Garden Banks

The Flower Garden Banks (FGB) is a coral reef ecosystem located approximately 100 miles off the Texas-Louisiana coast. It was first discovered by fishermen in the early 1900's, who named the banks after the colorful corals, sponges and fish they observed below the boat. The FGB is now protected by the National Oceanic and Atmospheric Administration (NOAA) and is the only national marine sanctuary in the Gulf of Mexico. It consists of three banks: East Flower Garden Bank, West Flower Garden Bank and Stetson Bank (Figure 7).

Texas A&M led early efforts to research and protect the banks, and the FGB is considered to be one of the healthiest coral reef ecosystems in the Gulf of Mexico and Caribbean Sea. However, the FGB is threatened by stressors including invasive species, ocean warming and ocean acidification, all of which will cause ecosystem health to decline.

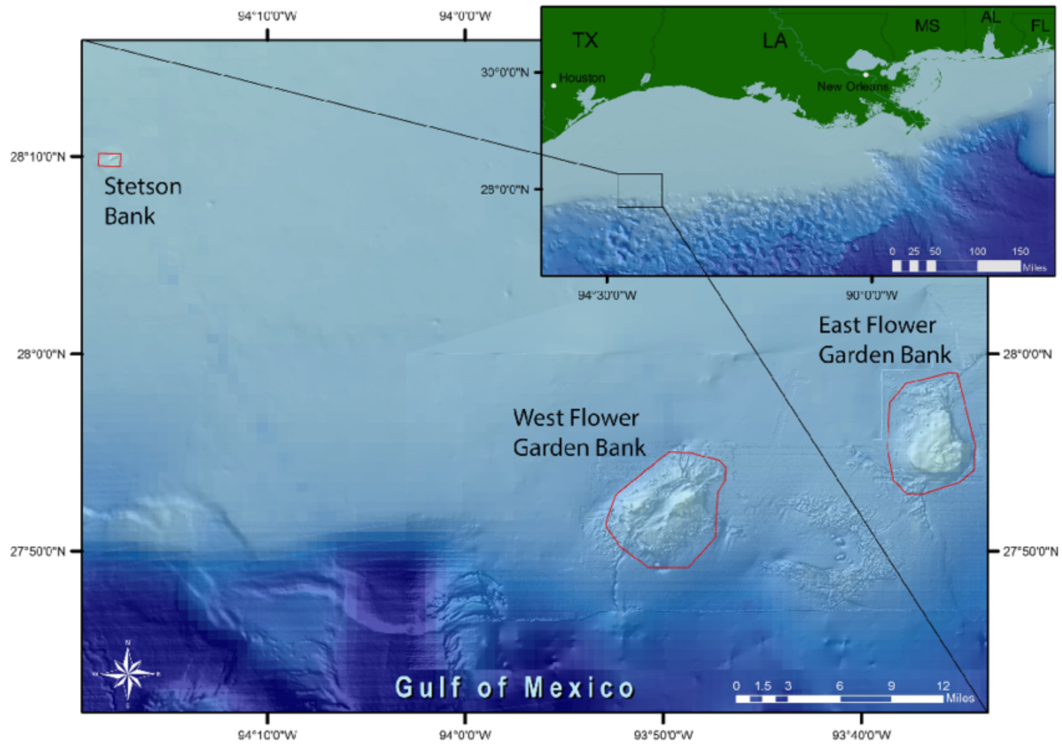

Figure 7: Map of the East Flower Garden Bank, West Flower Garden Banks and Stetson Bank located on the Texas-Louisiana continental shelf (Johnston et al. 2016).

EXERCISE 4: *Explore the Flower Garden Banks*

Take a virtual dive into the Flower Garden Banks National Marine Sanctuary.

1. Visit https://sanctuaries.noaa.gov/vr/flower-garden-banks/ and click on “Bleaching, algae, and a lionfish, OH MY!”.

2. Toggle through the scene to get a 360° view.

Answer the following questions:

A. In addition to ocean acidification, corals reefs are threatened by ocean warming, which causes coral bleaching. What is coral bleaching and how does it harm corals?

B. Identify the lion fish in the scene. Why are lionfish harmful to the FGB?