

## Measuring Greenhouse Gases in Aquatic Environments

Natural environments such as lakes, rivers, forests and peatlands, emit greenhouse gases (GHG). In general, following the impoundment of a hydroelectric reservoir, there is a rapid increase in net gas emissions mainly due to the degradation of the organic matter flooded by bacteria. The current project consists of evaluating net GHG emissions from Eastmain-1 reservoir, compared to the neighboring natural environments and to follow the evolution of emissions over time. Carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) are the main GHG being measured.

GHG emissions from a body of water can be estimated by measuring either:

- the **concentrations** of gases dissolved in the water, or
- the gas **fluxes** between the atmosphere and the water from the reservoir.

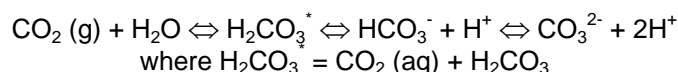
### Measuring the concentration of gas (CO<sub>2</sub> and CH<sub>4</sub>) in the water column

There are three main techniques for measuring the concentration of gas dissolved in water, i.e., the quantity of gas per water volume unit:

#### 1. Chemical method based on pH, alkalinity and temperature

Inorganic carbon is composed of 4 dissolved species: dissolved CO<sub>2</sub> (CO<sub>2</sub> (aq)), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>). The concentration of H<sub>2</sub>CO<sub>3</sub> is minimal (~1/390th) compared to that of CO<sub>2</sub> (aq) and, by convention, their sum is called "free CO<sub>2</sub>" and symbolized by H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>.

The three reactions involving the carbonates can be summarized as follows:



Gaseous CO<sub>2</sub> readily dissolves in water to form aqueous CO<sub>2</sub>. Aqueous CO<sub>2</sub> reacts with water (hydrolysis) to form carbonic acid. Carbonic acid is a weak acid that dissociates into bicarbonate, which in turn dissociates into carbonate. The relative proportion of each of these carbonated species is determined solely by the environmental pH.

The equilibrium constant (K) of each of these 3 reactions can be estimated since it represents the quotient of the concentration of products over the concentration of reactants of the respective reactions. The temperature of the sample must also be noted since the equilibrium constant varies slightly according to the temperature.

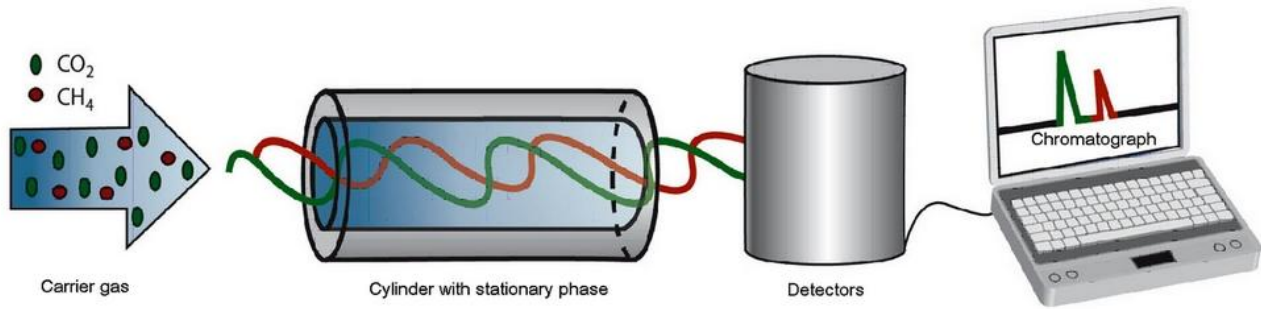
Thanks to a titration curve, we can measure the alkalinity of the water, i.e., its capacity to neutralize H<sup>+</sup> ions. We can then deduct from this information the total concentration of inorganic carbon.

Depending on the pH, the temperature and the total concentration of inorganic carbon, by reorganizing the terms of the equation, we can calculate the relative proportion of the 3 carbon species as well as their concentration in a sample of water.

#### 2. Gas Chromatography (GC)

A water sample is collected on site. In the laboratory, the gas dissolved in the water is transferred, by mechanical mixing, into a known volume of air. This air is then analyzed using a chromatograph in order to separate and quantify the different components of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>). To do this, the air sample is first vaporized in a heated room. Once vaporized, the different components are transported by the carrier gas through a column containing a solid substance called the stationary phase. Each of the sample's constituent molecules will be separated and will exit the column in series depending on their affinity with the stationary phase.

The nature of the components is determined by the time it takes for the peak to appear (retention time), whereas the concentration is represented by the peak area (area below the curve).



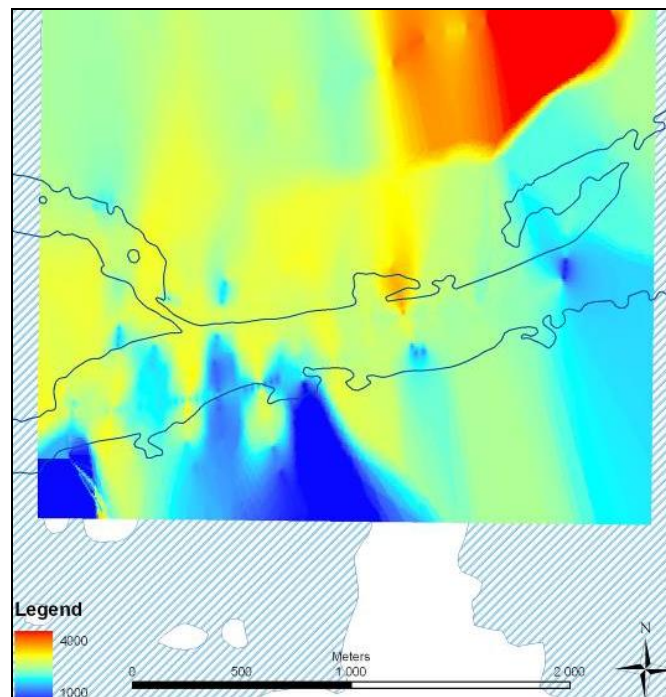
**Figure 1:** Diagram of gaseous-phase chromatography equipment.

### 3. Infrared gas analyzer EGM

A degasser (Liqui-Cel® MiniModule) is used to extract the CO<sub>2</sub> from the water. The water circulates in a room filled with capillaries whose walls are made of a hydrophobic membrane which lets the gas through but not the water. A vacuum is created, allowing the CO<sub>2</sub> to leave the liquid phase and enter the gaseous phase.

CO<sub>2</sub> concentrations are then measured instantaneously and precisely by an infrared analyzer EGM-4 (environmental gas monitor for CO<sub>2</sub>, PPSystems). Gases made up of two-atom molecules, such as CO<sub>2</sub>, readily absorb photons in the infrared specter. The quantity of photons associated to this wavelength measured by the EGM is hence inversely proportional to the quantity of CO<sub>2</sub>.

In addition to statistical data (for a precise location), it is possible to obtain georeferenced data, recorded continuously, which allow us to map the concentrations of CO<sub>2</sub> for an entire environment.



**Figure 2:** Example of a georeferenced map of CO<sub>2</sub> concentrations for a portion of Eastmain-1 reservoir.

## Calculating gas exchanges with the atmosphere (flux)

Gas exchange theory postulates that flux is governed by two phenomena: the partial pressure difference between water and the atmosphere and the coefficient  $k$ , which is the speed of gas exchanges. Many factors can influence  $k$  such as: wind speed, waves, temperature, rain or the presence of a surfactant. There are 4 methods for measuring GHG fluxes between the aquatic environment and the atmosphere.

### 1 Calculation based on the concentration of $\text{CO}_2$ measured in the water

Gas exchange by diffusion between water and the atmosphere can be modeled according to Flick's first law, where the flux is proportional to the concentration gradient (partial pressures) across an interface. First of all, the flux is in the direction of the gas's partial pressure gradient, from the highest partial pressure to the lowest. Second, the speed of the exchange is described by the gas exchange coefficient  $k$ , according to the following relation:

$$F = k \cdot Kh (p\text{CO}_2_{\text{water}} - p\text{CO}_2_{\text{air}})$$

The flux ( $F$ ) of a given gas represents the quantity of gas emitted per unit surface and unit time. Henry's law constant ( $Kh$ ) allows us to convert the partial pressure of the gas ( $p\text{CO}_2$ ) into concentration depending on the temperature and salinity of the water. The coefficient  $k$  represents the speed of gas exchange which is influenced by the water's meteorological, as well as biological and physicochemical conditions.

### 2 Inert gas tracer (sulfur hexafluoride, $\text{SF}_6$ )

This method involves measuring the evasion of a biologically inactive gas tracer such as  $\text{SF}_6$ . By following a known quantity of gas ( $\text{SF}_6$ ) which was added to the system, one can then calculate, by mass balance, the rate of gas evasion. This method provides data on gas transfer speed on a temporal scale of one day to a few weeks, depending on the thickness of the layer of water which is mixed and the rate of the gas transfer, and on a spatial scale ranging from a small body of water to a very large one (approximately 450 km<sup>2</sup>).

### 3 Eddy Covariance Technique

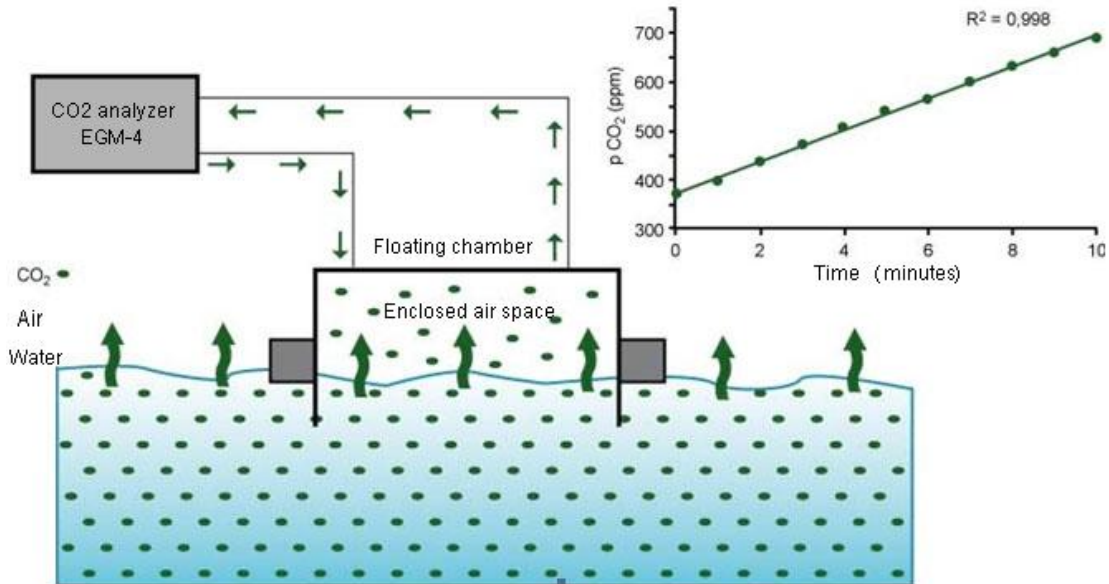
This technique uses complex instruments installed at the top of a tower, which allow us to precisely and continuously measure the partial pressure of  $\text{CO}_2$  in the air (infrared gas analyzer IRGA) as well as wind speed in 3 dimensions (three-dimensional sonic anemometer). The concept is simple: when the vectors of upward wind speed (from the water to the sky) are coupled with a higher concentration of  $\text{CO}_2$  than that of downward wind speed (sky to water), then the aquatic environment is acting as a source of  $\text{CO}_2$  and we can calculate the ascending flux of gas measured by the signal. The quantity of  $\text{CO}_2$  emitted by the surface under study is based on the covariance between vertical wind speed and gas concentration. The advantage of this method is that it allows us to cover a large area over a relatively small temporal scale (1/2 hour).



**Figure 3:** Eddy covariance tower located on an island on the Eastmain-1 reservoir.

#### 4 Floating chamber

The floating chamber is an economical method that requires minimal logistical effort (easily transportable) and allows for punctual and localized flux measures. This method measures the gas accumulation rate in a closed compartment (chamber) floating at the surface of the water and linked to an infrared gas analyzer (EGM-4) over a given span of time. Generally, placing the chamber on the surface of a body of water for ten minutes is sufficient to obtain an accumulation rate with a coefficient of determination ( $R^2$ ) that is often higher than 0.95.



**Figure 4:** Diagram of the floating chamber method with an example of a typical regression of the accumulation of the pCO<sub>2</sub> in the chamber over time.

Each of the methods for measuring GHG emissions from Eastmain-1 reservoir described above has its advantages and limitations. One of the aquatic team's objectives in this project is to compare the results obtained from the various techniques. The final step will be to develop empirical models, based on the integration of these results, from which we can extrapolate data for all of Eastmain-1 reservoir.

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