STANDARD OPERATING PROCEDURE

Measurement of Greenhouse Gas Concentration in Shrimp Farms Using the Headspace Method

Version	1.1	**Date of Issue**	02/12/2025
Purposes	This Standard Operating Procedure (SOP) displays the headspace method for the measurement of dissolved greenhouse gas concentration from shrimp farm ponds. With relatively modest infrastructure investments, measurement may be attained from multiple treatments/locations and over timeframes ranging from minutes to hours.		
Scope	The headspace (HS) method is a low-cost and simple method frequently used to determine dissolved gas concentrations from waters. This method can be either combined with semi-empirical equations (Thin boundary layer-TBL) to determine point measurements of diffusive fluxes, or used to determine profiles of the variation of gas concentration in the water column. If the sampling objective is to calculate diffusive fluxes, water samples should be collected at the water surface, while for determining the dissolved gas profile, water samples can be taken at various depths.		
Requirements	Some information needs to be defined before the measurement: • Define measured gas concentration • Define measured waterbody • Define the equipment that will be used to process water samples (gas chromatography type and specifications) • Define sites of interest including spatial resolution of measurements and number • Define timeframe of measurements		
Related documents	1. IHA, *GHG Measurement Guidelines for Freshwater Reservoirs: Derived from: the UNESCO/IHA Greenhouse Gas Emissions from Freshwater Reservoirs Research Project*. 2010: International Hydropower Association (IHA). 2. Eggleston, H., et al., *2006 IPCC guidelines for national greenhouse gas inventories.* 2006. 3. APHA, *Standard methods for the examination of water and wastewater.* American Public Health Association (APHA): Washington, DC, USA, 2005.		

Procedure

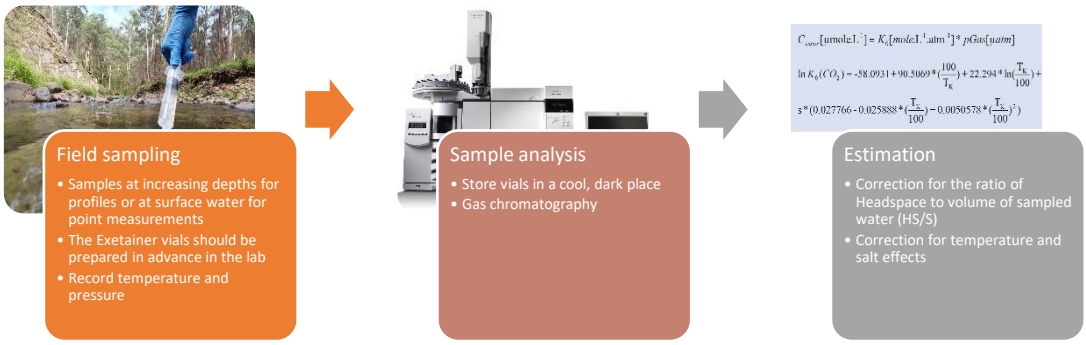

Figure 1. Measurement procedure of dissolved greenhouse gas concentration from shrimp farms using the headspace method

Step 1: Field sampling	For determining gas concentration profile, water samples are collected at various depths at a specific station of interest. In this case, a gas-tight container should be used to collect water samples (e.g. Kemerrer, Van Dorn or Niskin sampler). When the end goal is to calculate diffusive fluxes, water samples should be collected at the water surface by using a syringe. The volume of water collected must be defined in advance based on the type and specifications of the equipment that will be used to calculate the dissolved gas concentration. The HS can be created before going to the field or just before analysis. In the former case, closed Exetainer vials/bottles are prepared in the lab, flushing them several times with inert gas, such as helium (He) or nitrogen (N_2) [1]. The dissolved GHG sample is taken using the headspace method. The protocol can be slightly varied according to the equipment of each participant but the suggested method is: 1. Flush a 60ml syringe several times with atmospheric air in the field. 2. Take 30ml of atmospheric air from approximately 1m above the water surface into the syringe. 3. Put the syringe just under the pond/ditch water and take 30ml of pond/ditch water into it. 4. Close the stopcock and shake the syringe vigorously for 60 seconds. 5. Attach a needle to the stopcock, open the stopcock, and inject the headspace air into a pre-evacuated vial for GHG analysis (i.e. so the pond/ditch water remains in the syringe). The exact amount of headspace air injected will depend on each participant's analysis protocol (e.g. gas chromatography, GHG analyser equipped with sampling loop). 6. Steps 1-5 may need repeating if you need multiple samples to analyse different GHG by different methods (e.g. if you plan to measure N_2O on a gas chromatograph but CO_2 and CH_4 on a gas analyser). In both cases the water temperature and atmospheric pressure must be noted for calculations. Samples must be stored in a cool, dark place (e.g. in a cooler) until the analysis is done.

Step 2: Sample analysis	Exetainer vials with collected gas samples should be measured in the lab following the guideline of APHA [2]. Details of the standard methods for gas analysis measurement, including volumetric and gas chromatographic methods, can be found in this guideline.
Step 3: Flux estimation	The results of HS using the gas chromatograph (HS-GC) must be corrected for the ratio of HS to volume of sampled water (HS/S) partitioning of gases [1,3]. The concentration of gas dissolved in the water (C_{water}) is obtained by the product of gas partial pressure obtained from the HS-GC (p_{Gas}) times the gas solubility (K_0) at a given temperature (Eq. 1). For CO_2 the solubility of the gas on water will depend on the temperature and salinity, whereas for N_2O and CH_4 the solubility is only affected by temperature [1, 3]. $$C_{water}[\mu mole.L^{-1}] = K_0[mole.L^{-1}.atm^{-1}] * p_{Gas}[\mu atm] \ (Eq.1)$$

Quality management	
QA / QC procedures	The HS method is subject to following uncertainties and errors: (1) leaking from the septa cover and when using the syringe, (2) when preparing the HS in the lab, note that no vacuum is perfect and that a small amount of air will always remain in the vials which will affect measurements, (3) CH_4 adsorption on the container walls for which the use of clean borosilicate glass bottles or vials is recommended, along with septum stoppers that where baked for a few hours at 60°C to remove any trace of CH_4-producing chemicals, (4) the volume of HS plus S needs to be precisely determined for which it is recommended to weigh bottles when empty and then when filled with water, and calculate the mean volume using the density of water [1].

Version Log

Version	Authors	Material changes from previous version	Release Date
1.0	Long Ho	Initial version	02-12-2025

Bibliography

[1] IHA, *GHG Measurement Guidelines for Freshwater Reservoirs*. The International Hydropower Association (IHA), 2010. Accessed: Oct. 07, 2022. [Online]. Available: https://www.hydropower.org/publications/ghg-measurement-guidelines-for-freshwater-reservoirs

[2] APHA, *Standard methods for the examination of water and wastewater*. 1999.

[3] M. Koschorreck, Y. T. Prairie, J. Kim, and R. Marcé, "Technical note: CO_2 is not like CH_4 – limits of and corrections to the headspace method to analyse pCO_2 in fresh water," *Biogeosciences*, vol. 18, no. 5, pp. 1619–1627, Mar. 2021, doi: 10.5194/bg-18-1619-2021.

[4] R. F. Weiss, "Carbon dioxide in water and seawater: the solubility of a non-ideal gas," *Marine Chemistry*, vol. 2, no. 3, pp. 203–215, Nov. 1974, doi: 10.1016/0304-4203(74)90015-2.