



GHG Measurement Guidelines for Freshwater Reservoirs

Derived from:

The UNESCO/IHA Greenhouse Gas Emissions from Freshwater Reservoirs Research Project



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The Project has benefited from the collaboration of numerous research institutions and scientists within its peer-review group. The group was established through a series of international workshops convened over the past three years, and comprises representatives from more than 100 institutions, including universities, research institutes, specialist companies, sponsoring agencies, and others. All documents produced under the Project pass through the peer-review group before being published on the IHA and UNESCO websites.

These *GHG Measurement Guidelines for Freshwater Reservoirs* put together the main products developed under this consensus-based, scientific approach, and set the basis for the next stages of the research.

Further information on the Project's work can be found at: www.hydropower.org

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1. Executive summary

1.1 Introduction

1.2 Summary of individual sections

1.3 Next steps



1. Executive summary

1.1. Introduction

1.1.1. Background

Mitigating climate change is one of the most important goals for strategic sustainable development. There is a clear and pressing need to quantify the greenhouse-gas (GHG) footprint of all human activities. The GHG status of freshwater reservoirs – that is, any change in GHG emissions in a river basin resulting from the creation of such a reservoir – has been mentioned in both scientific and policy forums.

Quantification of the GHG status of a reservoir requires consideration of exchanges before and after its construction. However, there has been no scientific consensus on how in fact to go about measuring the GHG status of freshwater reservoirs.

This lack of consensus has impeded progress in decision-making on specific activities. For example, scientific guidance is needed to support the construction of national GHG inventories; develop methods (measurement and predictive modelling) of establishing the GHG footprint of new water infrastructure projects; and to quantify more precisely the carbon offsets of hydropower projects for GHG emission trading. More generally, policy making on energy, water and climate action is compromised by the current lack of understanding. This has a global impact on planning, especially in developing countries.

Despite strong efforts to build consensus in assessing the GHG status of reservoirs, many uncertainties have remained. Specific problems have been the lack of standard measurement techniques, limited reliable information from a sufficient variety of sources, and the lack of standard tools for assessing net GHG exchanges from existing and planned reservoirs.

These circumstances led to consultation between scientists and the International Hydropower Association (IHA) and UNESCO's International Hydrological Programme, and the subsequent launch of the UNESCO/IHA GHG Status of Freshwater Reservoirs Research Project (the Project). The Project, hosted by IHA in collaboration with UNESCO, aimed to improve understanding of the impact of reservoirs on natural GHG emissions and of the processes involved, and to help fill knowledge gaps in this area.

After several years of preliminary work, the Project began in August 2008. Its goals and purposes were set by two previous scientific workshops hosted by UNESCO (in 2006 in Paris, France and in 2007 in Foz do Iguaçu, Brazil), as part of the UNESCO International Hydrological Programme phase VI (IHP-VI) 2002-2007 work programme. These events were followed by a meeting in Paris in January 2008, which finalised the state-of-the-art paper *GHG Status of Freshwater Reservoirs – Scoping Paper* (Tucci et al., UNESCO/IHA; April 2008).

The Project's main goals were identified as:

- developing, through a consensus-based, scientific approach, detailed measurement guidance for net GHG assessment;
- promoting scientifically rigorous field measurement campaigns, and the evaluation of net emissions from a representative set of freshwater reservoirs throughout the world;
- building a standardised, credible set of data from these representative reservoirs;
- developing predictive modelling tools to assess the GHG status of unmonitored reservoirs and potential sites for new reservoirs; and
- developing guidance and assessment tools for mitigation of GHG emissions at sites vulnerable to high net emissions.

The Project has benefited from a consensus-based, scientific approach involving collaboration among many research institutions and scientists. All the resulting deliverables have been reviewed by the Project's peer-review group, which comprises some 160 researchers, scientists and professionals working in this field, from more than 100 institutions, including universities, research institutes, specialist companies and sponsoring agencies.

Since the Project began in August 2008, three workshops have been convened, under the scope of UNESCO IHP-VII (2008-2013), and a variety of written deliverables produced. These have been integrated to form the *GHG Measurement Guidelines for Freshwater Reservoirs* (the *Guidelines*), comprising five sections:

- Executive summary
- Concepts and processes
- Field Manual
- Calculation Manual
- Glossary.

1.1.2. Objectives and application of the *Guidelines*

The *Guidelines* are for planning and conducting measurement campaigns to estimate net GHG emissions from freshwater reservoirs before and after their construction. They aim to ensure that assessments are objective, and to make it easier to compare, transfer and use data globally (subject to rules of access). They also aim to promote scientifically sound evaluation of the GHG exchange resulting from freshwater reservoir construction.

The *Guidelines* are intended to apply worldwide, for all climate types and reservoir conditions, and for freshwater reservoirs of all types and purposes. As part of the UNESCO/IHA GHG Research Project, the *Guidelines* are intended for assessing GHG emissions in a sample of representative sites throughout the world. Data from this initiative will help improve predictive capacity.

The *Guidelines* are not meant as a general method for routine assessment and monitoring in existing and future reservoirs. Rather, they propose a standard method to allow easier comparison and transfer of detailed field data collected from comprehensive research studies on reservoirs and watersheds, looking at all the underlying processes and their relative significance. So the Project's ultimate goal is to develop predictive modelling tools that can replace the intensive monitoring requirements described in this Publication. These modelling tools would apply to reservoirs in general, and would thus reduce the need to perform the evaluations proposed in this version of the *Guidelines*.

The present version was developed to provide the standards for assessing net GHG emissions in a representative set of reservoirs. At the end of this measurement programme, the available data may justify a two-tier approach to assessment in the future:

1. assessments of key parameters to check whether there are likely to be significant emissions;
2. if necessary, more intensive monitoring to quantify the net GHG emissions.

This tiered approach makes the *Guidelines* relevant in assessing emission estimates for several different uses including carbon trading mechanisms; developing national GHG inventories; complying with national environmental requirements; assessing the GHG status of

new reservoir sites and of existing unmonitored reservoirs; planning mitigation; and carrying out scientific research.

The *Guidelines* are being developed as a 'living document'. As further experience is gained and uncertainties are reduced, they will be updated with new information.

For each reservoir to be analysed and its net GHG emissions estimated, it is necessary to go through several steps in data analysis, for both pre- and post-impoundment conditions. Figure 1.1 shows this iterative process, including verification of adequacy of the available data and possible need to redesign the space and time distribution of the field and laboratory point measurements.

1.2. Summary of individual sections

As stated above, each time an assessment is done, the process will include several iterative steps as described in Figure 1.1. The process will include verifying the adequacy of the data. Each section's role in the process is described below.

1.2.1. Concepts and processes

This section aims to provide the theoretical basis for producing guidance for standardised measurements, seeking to ensure objective assessments and make it easier to compare, transfer and use data globally.

The main elements of the section are as follows:

General principles and data

- Introduces the inland waters component of the carbon cycle and the generally available data.
- Describes previous work, and introduces the main principles for taking GHG measurements from reservoirs.
- Considers key processes and parameters, stressing the importance of considering net emissions; the need for pre- and post-impoundment assessments; and the role of carbon and nutrient loading from the catchment, from natural and unrelated human activities.

Spatial and temporal resolution of sampling

- How seasonal changes in climate, reservoir operations and carbon load may affect the temporal resolution.
- Where and when to measure, taking into account vegetation and pre- and

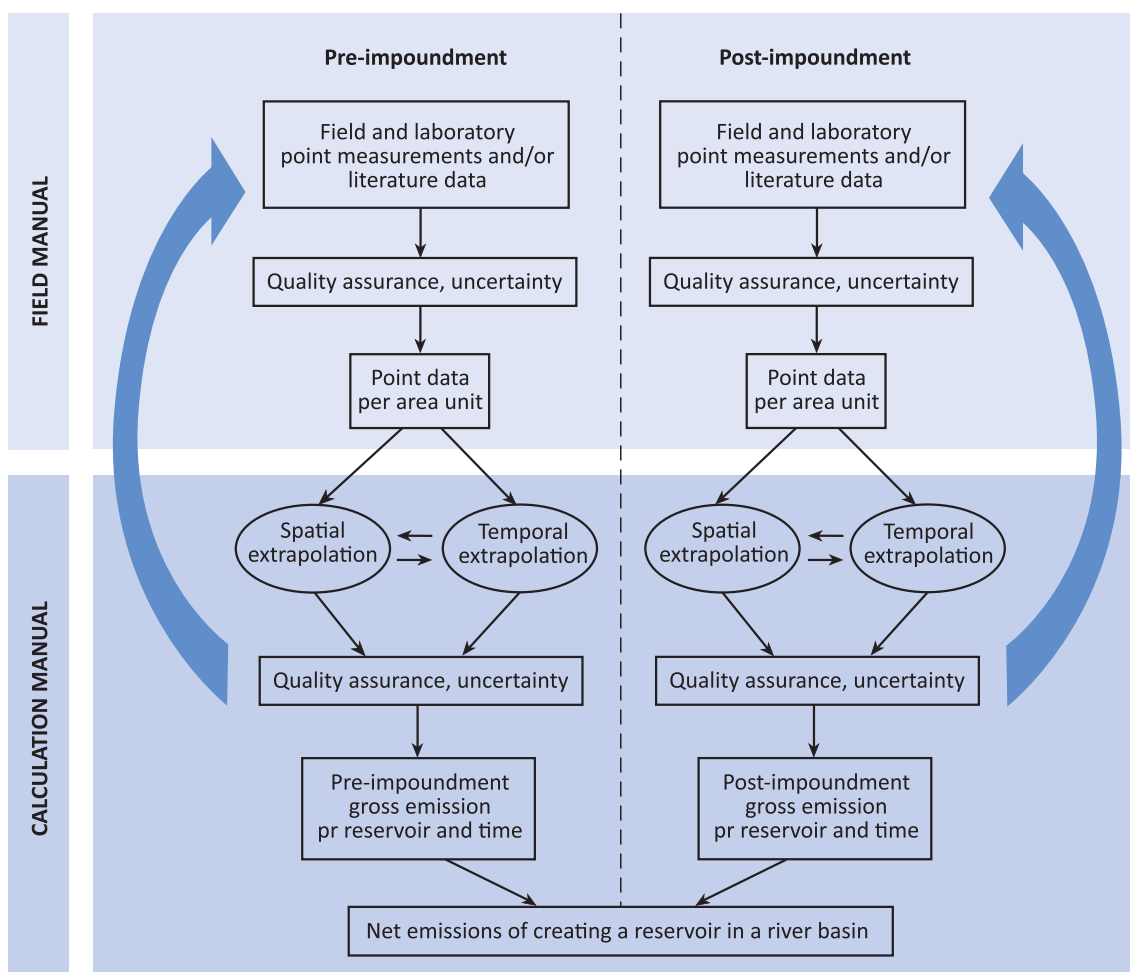


Figure 1.1: General schematics for data analysis

post-impoundment land use; hydrological and water-quality issues; and other anthropogenic activities; as well as practical issues like accessibility, safety and other indirect implications.

Methods and equipment

- What to measure, how to measure and a general description of the main equipment for measuring carbon (carbon cycle), GHG emissions, carbon storage in sediments, and physical and water-quality parameters, highlighting advantages and constraints.

Detailed descriptions of the procedures and recommended equipment are presented in the *Field Manual*.

1.2.2. Field Manual

The *Field Manual* provides instructions on the field methods and equipment necessary to estimate GHG emissions. It gives qualified technicians and scientists a protocol to make GHG emission measurements in the field. More specifically, the

Field Manual includes instructions on how to conduct GHG measurements in terrestrial (forest, grass and peatland) and aquatic (wetland, lake, river and reservoir) ecosystems in terms of GHG emissions and carbon and nitrogen stocks.

The main sections of the *Field Manual* are as follows:

Sampling considerations

- The approach to estimating the net GHG emission rates from reservoirs.
- Steps and principles in planning field surveys.
- How to determine the sampling effort, spatial and temporal resolution for sampling and considerations for young and mature reservoirs and for anthropogenic inputs.
- How to estimate GHG emissions when pre-impoundment measurements are or are not available.

Terrestrial system methods

- Variables to be measured.

- Instruments for estimating terrestrial emissions, including GHG measurements and carbon and nitrogen stock assessments.

Aquatic systems methods

- Variables to be measured.
- Instruments for estimating aquatic emissions, including GHG measurements and carbon and nitrogen stock assessments.

Gas analysers and gas measurement technologies

- Brief review of gas analysers, including gas chromatography (GC) analysis, infrared gas analysers (IRGAs) and automated systems.

Ancillary measurements

- Associated measurements.
- Standard protocols for water quality, physical water variables and climatic conditions.

Quality assurance and quality control

- General quality assurance and quality control (QA/QC) tools. Specific QA/QC items are included in the specific method when required.

1.2.3. Calculation Manual

The *Calculation Manual* presents the standard procedures required to calculate net GHG emissions resulting from the creation of a reservoir in a river basin. The manual is designed to be used with the data obtained from the procedures described in the companion *Field Manual*.

The main sections of the *Calculation Manual* are as follows:

Spatial extrapolation of gross GHG field data

- How to extrapolate from point sample estimates to areal units, estimating the mean or total values of the measured emissions in the system (and the associated variances).
- How to integrate all the points to estimate the gross (total) GHG emissions from the whole area of interest.

Temporal integration

- How to ensure compatibility of the results with the temporal integration of the available data.
- How to allow for inter-annual variability, seasonal variability and nycthemeral variations.

Adequacy analysis of the spatial and temporal resolution

- Analysis of the adequacy of the available field data to be used to perform a net GHG calculation.

- Re-evaluation of the monitoring programme.
- Internal adequacy analysis.
- Comparison to external references.
- Changes in pre-impoundment assessments, and in post-impoundment measuring design.

Calculation of net emissions

- Estimation of emissions.
- Boundaries and their direct and indirect impacts on emissions.
- Carbon stock changes.
- Integration of different results (gas species, pathways, monitored areas, integrated emissions, carbon fluxes and carbon stock).
- Upscaled to 100 years.
- Calculation of net GHG emissions by comparing pre- and post-impoundment conditions.

Evaluation of uncertainties

- The main issues for evaluation of uncertainties in assessing the change in GHG emissions resulting from the creation of a reservoir.
- Variability, transparency and natural, intrinsic or fundamental uncertainty, as well as technical or form uncertainty, including sampling and error analysis.
- Model uncertainty and error propagation.

Final presentation of results

How to present the results, including which variables to cover and which units to adopt.

1.3. Next steps

The Project is pioneering a first step towards standardising equipment and procedures to accurately evaluate the net GHG impact of freshwater reservoirs. The *Guidelines* describe the required standard procedures, evolved through a consensus-based approach, that are now ready to be applied in a range of reservoirs to help get representative, comparable and transferable data that will allow scientifically sound evaluation of the GHG footprint of these reservoirs.

The next steps include:

- promotion of field measuring programmes in compliance with the proposed method;
- capacity-building training programmes for taking such field measurements;

- development of predictive modelling tools to assess the GHG status of unmonitored reservoirs and potential new reservoir sites;
- development of guidance and assessment tools to mitigate GHG emissions at vulnerable sites.

As the Project has progressed, the importance of a capacity-building training programme has been identified. Such training would ensure a proper understanding and application of the standard procedures developed under the Project. This, in turn, would provide enough data to allow the science to move forward and build the necessary predictive modelling capacity.

An essential next step is to develop adequate predictive modelling tools to assess the GHG status of unmonitored reservoirs and potential sites for new reservoirs. These tools, once validated, could provide the basis for developing appropriate guidance on national GHG inventories, and to quantify carbon offsets at the project level, without the need for specific field measurement programmes.

It is important to carry forward the UNESCO/IHA forum process, including workshops and peer-review evaluation. The process is costly in time, resources and money and those who take part mainly do so as volunteers. It makes a crucial contribution to reinforcing the strong, transparent, consistent approach that the Project needs.

2. Concepts and processes

2.1 Introduction

2.2 General principles and data

2.3 Spatial and temporal resolution of sampling

2.4 Methods and equipment

2.5 References



2.1. Introduction

2.1.1. Background

The assessment of the *GHG Status of Freshwater Reservoirs: Scoping Paper* (UNESCO/IHA, 2008) has been used as a key reference in drafting this document as it represents the state of the art on this subject.

According to UNESCO/IHA (2008), freshwater reservoirs are used to regulate flow for many purposes, including water supply, irrigation, flood mitigation, drought protection, navigation and hydropower. Flux measurements above the water surfaces of flooded land have indicated that changes in the emission of carbon dioxide, methane and nitrous oxide may occur at levels that are relevant to inventories of greenhouse gas (GHG) exchanges. Research suggests that emission levels in cold and temperate climates are generally low, but may be high in some tropical systems with persistent anoxia (e.g., Tremblay et al. 2005). However, it is important to improve the available information about the GHG status of existing and new reservoirs and to provide the tools needed to support sound decision making on the mitigation measures that may be necessary.

To quantify the net GHG exchange in a river basin caused by the creation of a reservoir, it is necessary to consider exchanges before, during and after the construction of the reservoir. The difference between pre- and post-reservoir emissions from the portion of the river basin influenced by the reservoir will indicate the net GHG emissions of the reservoir. In accordance with IPCC (2006), the lifecycle assessment period for net GHG emissions is 100 years. For the purpose of this document, 'net lifecycle GHG emissions' is taken as a proxy for the carbon footprint of the reservoir.

Limited published data from tropical reservoirs indicates that GHG emissions vary among reservoirs, and also within each reservoir. This variation may have many causes, including carbon/nutrient loading from the catchment; temperature; oxygen concentration; type and density of the flooded vegetation; aquatic flora and fauna; residence time; wind speed; thermal structure; reservoir topography and shape; and water level.

2.1.2. Objectives and application

The objective of this section on Concepts and Processes is to provide the theoretical basis for guidance on standardised measurements to assess net GHG emissions associated with reservoirs¹.

The *Guidelines* are to be used to plan and conduct measurement campaigns to estimate net GHG emissions from freshwater reservoirs before and after their construction, aiming to ensure objective assessments and make it easier to compare, transfer and use data globally (subject to rules of access). They aim to promote scientifically sound evaluation of the GHG exchange caused by the construction of a freshwater reservoir.

Since 2008, UNESCO and the International Hydropower Association (IHA) have been hosting an international research project that aims to improve understanding of how reservoirs affect natural GHG emissions through clarifying the processes involved and helping to overcome knowledge gaps. The project's overall objective is to enable scientists to evaluate the carbon footprint (net GHG emissions) resulting from the construction of a freshwater reservoir within a river basin, as well as to identify potential mitigation measures. The project thus aims to:

- develop, through a consensus-based, scientific approach, detailed guidance on measurement for net GHG assessment;
- promote scientifically rigorous field measurement programmes, evaluating net emissions from a representative set of freshwater reservoirs throughout the world;
- build a standardised, credible set of data from these representative reservoirs;
- develop predictive modelling tools to assess the GHG status of unmonitored reservoirs and potential new reservoir sites; and
- develop guidance and assessment tools to mitigate GHG emissions at vulnerable sites.

As part of the UNESCO/IHA GHG research project, these *Guidelines* are intended for use in assessing GHG emissions in a sample of representative sites worldwide. Data produced from this initiative will

¹ The term 'reservoir' is understood as defined in the UNESCO/WMO International Glossary of Hydrology (1992): 'body of water, either natural or man-made, used for storage, regulation and control of water resources'. The glossary is the result of a comprehensive worldwide consultation of hydrological experts. There is no global consensus that 'reservoirs' are necessarily man-made, which is why these *Guidelines* use the expression 'man-made'.

help improve predictive capacity on this issue. For vulnerable sites, potential mitigation measures can be developed in the future.

These *Guidelines* are to be applicable worldwide, for all types of climate and different reservoir conditions, and for reservoirs of all types and purposes. Freshwater reservoirs have several different purposes, but the GHG-related processes are similar regardless of the purpose. However, reservoirs with low-level outlets (such as turbines, gates and valves), can exhibit the GHG pathway referred to as *degassing* (see Section 2.4.1.2.3).

Measurements should include all three of the identified GHG species:

- Carbon dioxide (CO₂) – according to the European Environmental Agency (EEA), CO₂ emissions account for the largest share of GHGs (equivalent to 80-85% of the emissions).
- Methane (CH₄) – emissions are significant, because reservoirs may create the conditions under which CH₄ can be produced and the global warming potential of CH₄ is 21 times stronger than that of CO₂ (UNFCCC, 100-year time horizon).
- Nitrous oxide (N₂O) – not enough is known about N₂O emissions to evaluate their importance; however, the global warming potential of N₂O is 310 stronger than that of CO₂ (UNFCCC, 100-year time horizon).

It is important to identify key processes and parameters. Determining the relative importance of the different processes helps to identify the main drivers of GHG emissions from reservoirs. Then attention can be focused on measuring the processes that effectively control the emissions. UNESCO/IHA (2008) identified key aspects of significant GHG emissions. However, their importance has to be tested under a comprehensive field measurement programme, as proposed in these *Guidelines*.

2.2. General principles and data

The main issues on the contribution, or potential contribution, of reservoirs as sources of GHG are the following:

- What is the GHG status of the river basin before reservoir impoundment?
- What is the observed range of fluxes of the major GHGs to and from the reservoir and the portion of river basin affected by the reservoir?

- What is the observed storage of carbon in the accumulating sediments, and the net primary GHG production of the reservoir and the portion of river basin it affects?
- What fraction of GHG fluxes and carbon storage results from the construction of the reservoir?
- If necessary, is it possible to reduce (mitigate) emissions from reservoirs, including those planned for the future?

The following sections introduce the inland waters component of the carbon cycle and the generally available data, including the main principles, and outline several different approaches. They also stress the importance of considering net emissions, with the need for pre- and post-impoundment assessments, and the role of carbon and nutrient loading from the catchment, arising from natural and human activities.

2.2.1. Previous work

Cole et al. (2007) estimate that inland waters receive, from a combination of background and anthropogenically altered sources, around 1.9 Pg C/year from the terrestrial landscape. Of this, about 0.2 Pg C/year is buried in aquatic sediments, while at least 0.8 Pg C/year (possibly much more) is returned to the atmosphere as gas exchange, and the remaining 0.9 Pg C/year is delivered to the oceans. Clearly, freshwater systems play a fundamental role in the natural carbon cycle.

In the last decade, freshwater reservoirs have been investigated as potential sources of CO₂ and CH₄ emissions to the atmosphere, in boreal (Rudd et al., 1993; Duchemin et al., 1995; Kelly et al., 1997; Huttunen et al., 2002; Tremblay et al., 2005), temperate (Therrien et al. 2005; Soumis et al., 2004, Casper et al. 2000) and tropical (Keller and Stallard, 1994; Rosa and Schaeffer, 1994; Galy-Lacaux et al., 1997, 1999; Delmas et al., 2001; Rosa et al., 2003; Abril et al., 2005; Sikar et al. 2005; Santos et al., 2006; Guerin et al. 2006; Kemenes et al. 2007) regions. GHG emissions from reservoirs at the global scale are subject to large uncertainties, and there is an urgent need for more observations and a better understanding of the processes involved. Simulation models are likely to be important in understanding and analysing the changes in GHG emissions that may occur due to the construction of a reservoir in a river basin (UNESCO/IHA, 2008).

Limited studies have estimated the significance of the net CO₂ balance of aquatic ecosystems compared to the CO₂ balance of terrestrial ecosystems at the basin scale. In some temperate and tropical catchments, CO₂ emissions from the aquatic ecosystems have been shown to be close to balancing the CO₂ uptake by the surrounding forest (Cole and Caraco, 2001; Richey et al., 2002).

Flux measurements at the water-atmosphere or land-atmosphere interface are often the only type of measurements reported in the literature. Few measurements of material transported into or out of the reservoir have been reported, and few studies have quantified carbon accumulation in reservoir sediments (UNESCO/IHA, 2008).

Age of the reservoir is an important issue. Younger reservoirs in the first years after impoundment need more measurements to capture the changes in emission rates and carbon stocks as the system adjusts. In boreal and temperate conditions GHG emissions have been observed to return to natural levels in less than ten years after impoundment (Tremblay, 2008). Further measurements (as proposed in this document) should reveal how quickly new reservoirs reach equilibrium under tropical conditions.

Fluxes of CO₂ and CH₄ have been measured in a limited number of boreal/temperate and tropical reservoirs (Table 2.1). Gross CH₄ emissions (see Section 2.2.3 for a further discussion on net and gross emissions) have been measured from South American reservoirs including four Amazonian sites (Balbina, Curuá-Una, Samuel, Tucuruí), and additional sites in central and

southern Brazil (Barra Bonita, Carvalho, Corumbá, Funil, Furnas, Itaipu, Itumbira, L.C.B., Manso, Mascarenhas de Moraes, Miranda, Ribeirão das Lajes, Serra da Mesa, Segredo, Três Marias, Xingó). Measurements are not available from reservoirs in other regions of the tropics or subtropics except for Gatun, Panama and Petit-Saut, French Guyana. For most of the studied reservoirs, two GHG pathways from the reservoir to the atmosphere have been researched: ebullition (bubbling) and diffusive fluxes from the surface of the reservoir. In addition, studies at the Petit-Saut, Samuel and Balbina reservoirs have investigated GHG emissions downstream of the dam. Measurements in boreal/temperate regions are available from Canada, Finland, Iceland, Norway, Sweden and USA (UNESCO/IHA, 2008).

2.2.2. Key processes and parameters

The identification of key processes and parameters leads to a better understanding of the mechanisms controlling GHG emissions associated with reservoirs. The following sections describe the key aspects of significant GHG emissions (UNESCO/IHA, 2008).

2.2.2.1. Carbon cycle in a natural catchment

In terrestrial ecosystems, the main source of carbon is atmospheric CO₂. The CO₂ is fixed by plants during photosynthesis for the primary production of organic matter (OM). A part of the produced OM is directly incorporated into the soil organic matter (SOM) via processes in the rhizosphere, or stored in the living biomass until the plant decays.

Table 2.1: Range of average carbon dioxide and methane gross emissions from freshwater reservoirs. (Source: UNESCO/IHA, 2008)

GHG pathway	Boreal & temperate		Tropical	
	CO ₂ mmol m ⁻² d ⁻¹	CH ₄ mmol m ⁻² d ⁻¹	CO ₂ mmol m ⁻² d ⁻¹	CH ₄ mmol m ⁻² d ⁻¹
Diffusive fluxes	-23—145 (107)	-0.3—8 (56)	-19—432 (15)	0.3—51 (14)
Bubbling	0	0—18 (4)	0	0—88 (12)
Degassing*	~0.1 (2)	n.a.	4—23 (1)	4—30 (2)
River downstream*	n.a.	n.a.	500—2500 (3)	2—350 (3)

* Numbers in parentheses are the number of reservoirs studied for each gas and each GHG pathway. The downstream emissions (generally in Mg d⁻¹) have been attributed to the surface of the reservoir to be expressed in the same units as the other fluxes (mmol m⁻² d⁻¹).

CO₂ and CH₄ can be produced under oxic and anoxic soil conditions. CH₄ can be oxidised by methanotrophic bacteria when diffusing from the anoxic part of the soil to the oxic part.

In well-drained 'upland' soils, aerobic CH₄ oxidation usually occurs (Conrad, 1989).

In 'lowland' or flood-plain soils, anoxic conditions may prevail and CH₄ production may be higher than CH₄ oxidation. Therefore, these soils may act as a source of atmospheric CH₄ (UNESCO/IHA, 2008).

Kepler et al. (2005) reported that CH₄ could be produced by plants in aerobic conditions. CH₄ has also been observed to be emitted from tropical forests. The occurrence and the extent of these processes remain unresolved (Houwelling et al., 2006; Kirschbaum et al., 2006; Dueck et al., 2007).

According to UNESCO/IHA (2008), the carbon (organic and inorganic) is transported in the aquatic system of the river basin (river, lakes and wetlands) by surface or subsurface runoff. The CO₂ and the dissolved inorganic carbon are consumed for

aquatic primary production or follow the pathways indicated in Figures 2.1 and 2.2. The CH₄ is oxidised in the soil and water column or emitted to the atmosphere. The OM, previously stored in the soils, may be released as CO₂ and CH₄. The fraction that is not emitted is stored in the aquatic system or exported downstream (Cole et al., 2007).

2.2.2.2. Pathways in reservoirs

According to UNESCO/IHA (2008), the source of carbon for the CO₂ and CH₄ is derived from:

- OM imported from the catchment;
- OM produced in the reservoir;
- decomposition of OM in plants and soils flooded by the reservoir.

CO₂ is produced in oxic and anoxic conditions in the water column and in the flooded soils and sediments of the reservoir, and is consumed by aquatic primary producers in the euphotic zone of the reservoir. CH₄ is produced under anaerobic conditions, primarily in the sediments; a portion will be oxidised to CO₂ by methanotrophic bacteria in

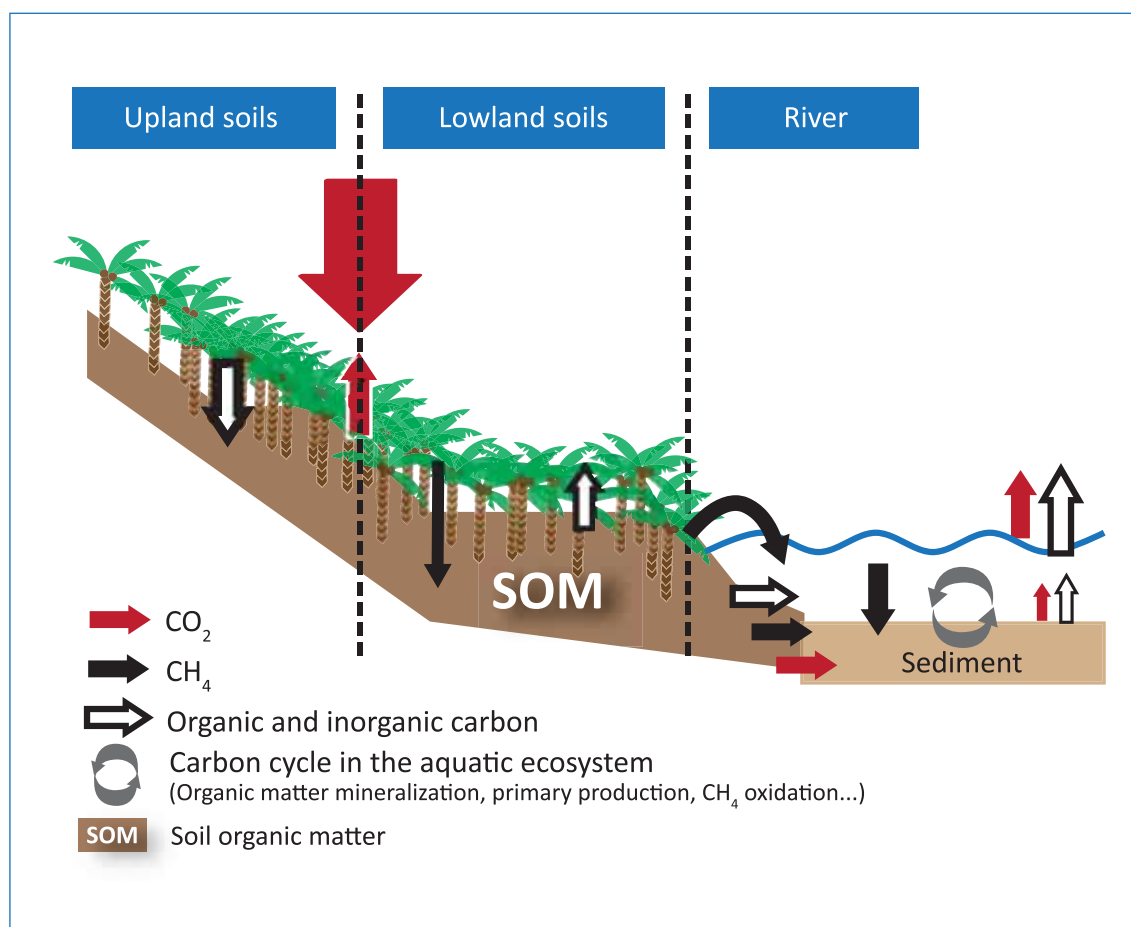


Figure 2.1: Carbon dioxide and methane emissions from a natural catchment (adapted from concepts in Conrad 1989 and Cole et al. 2007)

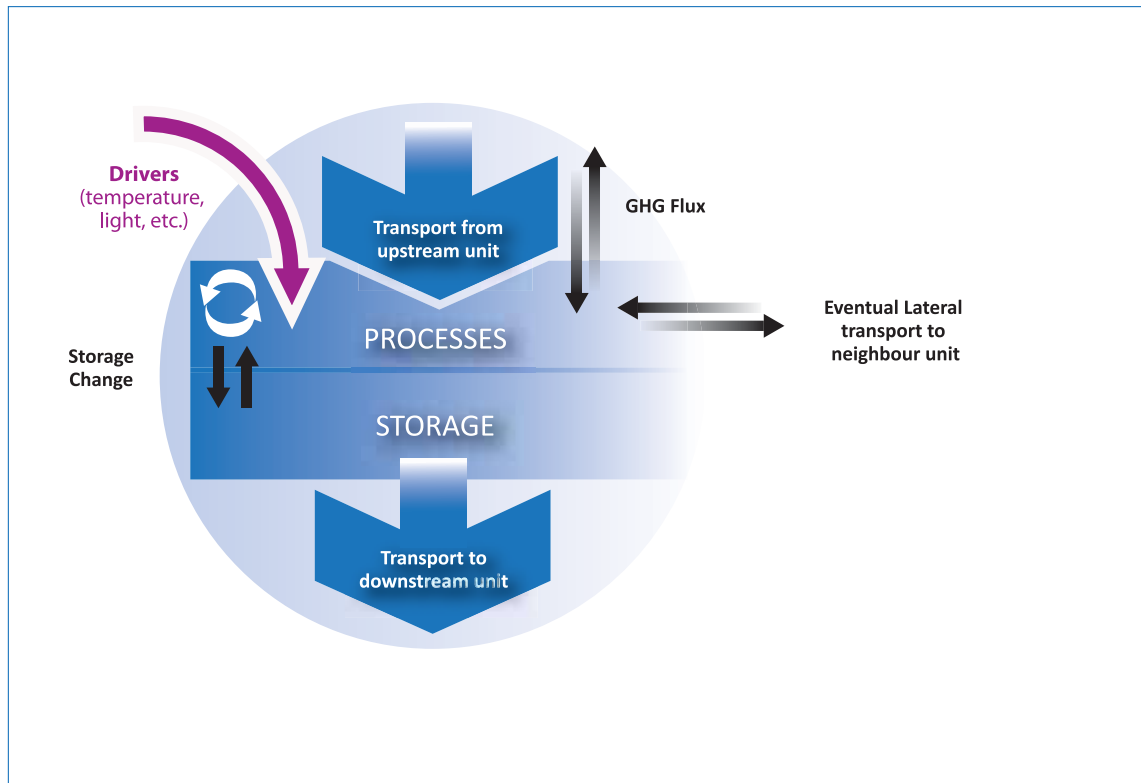


Figure 2.2: General concept for all units in a GHG emission study (adapted from UNESCO/IHA, 2008)

the water and sediments under aerobic conditions (Figure 2.3). Pathways for CH_4 and CO_2 emissions to the atmosphere from reservoirs include: (1) bubble fluxes (ebullition) from the shallow water; (2) diffusive fluxes from the water surface of

the reservoir; (3) diffusion through plant stems; (4) degassing just downstream of the reservoir outlet(s); and (5) increased diffusive fluxes along the river course downstream (Figure 2.3).

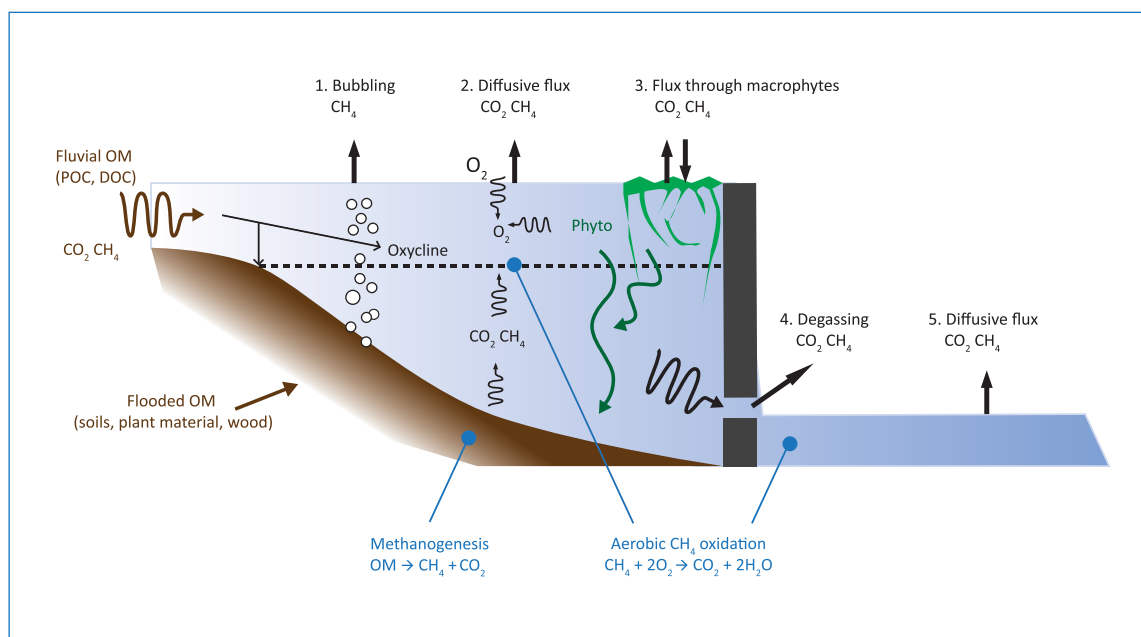


Figure 2.3: Carbon dioxide and methane pathways in a freshwater reservoir with an anoxic hypolimnion. For reservoirs with a well-oxygenated water column, methane emissions through pathways (2), (4) and (5) are reduced (adapted from UNESCO/IHA, 2008)

2.2.2.3. N₂O – main processes and pathways

N₂O is produced by both natural processes and human-related activities. Primary human-related sources of N₂O are agricultural soil management, animal-manure management, sewage treatment, mobile and stationary combustion of fossil fuel, adipic acid production and nitric acid production. N₂O is also produced naturally from a wide variety of biological sources in soil and water, particularly microbial action in wet tropical forests (USEPA, 2009).

N₂O is an intermediate by-product of two microbiological processes – nitrification (aerobic process) and denitrification (anaerobic process) – which occur mainly at the sediment/water interface but could also take place in organic-matter-rich water columns. Nitrification is an aerobic microbial process that converts ammonium (NH₄⁺) to nitrate (NO₃⁻) in the presence of oxygen. During denitrification, nitrates are transformed into nitrogen (N₂). Denitrification requires anoxic conditions, but denitrifying bacteria are facultative anaerobes (Schlesinger, 1997; Hahn et al., 2000).

The higher N₂O emission from tropical conditions could reflect the influence of temperature on nitrification and denitrification reactions, as well as nitrogen availability, which is greater in tropical than in boreal and temperate forests (Sitaula and Bakken, 1993; Stange et al., 2000; Clein et al., 2002).

There are still significant uncertainties about the contribution of the individual sources to atmospheric N₂O. Aquatic systems are considered to be significant, but not the dominant sources of atmospheric N₂O (IPCC, 1990). According to Mengis et al. (1997), N₂O concentrations seem to be strongly correlated with O₂ concentrations in lakes. In oxic waters below the mixed surface layer, N₂O concentrations usually increase with decreasing O₂ concentrations. N₂O is produced in oxic epilimnia, in oxic hypolimnia and at oxic-anoxic boundaries, either in the water or at the sediment-water interface. It is consumed, however, in completely anoxic layers. Anoxic water layers were therefore N₂O undersaturated. All studied lakes were sources for atmospheric N₂O, including those with anoxic, N₂O-undersaturated hypolimnia. However, compared to agriculture, lakes seem not to contribute significantly to atmospheric N₂O emissions (Mengis et al., 1997).

Few studies have measured N₂O fluxes in wetlands because the water-saturated and anoxic soils typical of these systems offer particularly

unfavourable conditions for N₂O production.

The nitrification rate is quite low in these systems because of very low oxygen content, pH and nitrogen availability (Bridgham et al., 2001). As for denitrification, it is often limited by the lack of nitrates, a direct consequence of slow nitrification rates (Regina et al., 1996).

There are indications that the contribution of N₂O to gross GHG emissions can vary from nearly 0 to 30% in some tropical reservoirs (Guérin et al., 2008). In boreal reservoirs, the information available to date indicates that the contribution of N₂O to gross GHG emissions is usually less than 1% (Tremblay et Bastien, 2009; Hendzel et al., 2005). Higher N₂O emissions may occur if there is a significant input of organic or inorganic nitrogen from the watershed, e.g., soils rich in ammonium (NH₄⁺) or nitrates (NO₃⁻), or anthropogenic activities such as agricultural (animal manure), urban (waste water and sewage treatment) or industrial (combustion, nitric acid production) activities.

2.2.2.4. Key processes

UNESCO/IHA (2008) identified the following aspects of GHG emissions.

Key processes influencing emission of GHGs to the atmosphere include the following:

1. Processes supplying organic carbon to the reservoir or its sediments:

- a. inputs of OM via groundwater, streams, transfer channels, tunnels and rivers (controlled by the discharge rate and the concentrations of OM in the catchment);
- b. net primary productivity of aquatic macrophytes, periphyton and phytoplankton growing in or on the water or in the drawdown zone around the reservoir, depending on the supply of nutrients and light;
- c. entrainment of terrestrial OM in living plants, litter and soils during impoundment;
- d. erosion of soil in the reservoir shore zone (adding OM to the reservoir and water bodies).

2. Processes producing conditions conducive to the production of GHG compounds:

- a. decomposition of flooded OM and the various types of OM entering the system, depending on the organisms present, temperature, dissolved oxygen and nutrients;

- b. photo-oxidation of dissolved organic carbon (DOC) (*Soumis et al., 2007*);
- c. aerobic oxidation of CH₄;
- d. nitrification and de-nitrification.
- f. biomass of plants, algae, bacteria and animals in the reservoir and drawdown zone;
- g. sediment load;
- h. stratification of the reservoir body.

3. Processes influencing the distribution of GHG compounds in the reservoir:

- a. mixing and transport processes that can lead to the movement of CO₂ and CH₄ to the surface;
- b. withdrawal via spillways and outlets;
- c. CH₄ oxidation in the water or sediments, depending on the physical stratification, dissolved oxygen, inhibition by light, nutrient levels and temperature;
- d. primary production in the euphotic zone of the reservoir water column, which consumes CO₂ and depends mainly on light and nutrient availability.

4. Pathways for the GHG compounds to move between the reservoir and downstream river, and the atmosphere:

- a. ebullition (bubbling);
- b. diffusive gas exchange between the atmosphere and the reservoir or downstream river;
- c. degassing immediately after water passes through turbines and in spillways;
- d. transport via aquatic plant stems.

2.2.2.5. Key parameters

Identifying key parameters controlling the emission processes can help to predict a reservoir's behaviour or its vulnerability to elevated GHG emissions.

The key parameters that control the rates of GHG emissions can be categorised as follows:

Primary parameters – creating GHG stock

Parameters that modulate the rates of biological processes such as OM production, respiration, methanogenesis and CH₄ oxidation:

- a. concentrations of dissolved oxygen;
- b. water temperature;
- c. OM storage, concentrations and C/N, C/P and N/P ratios in water and in sediments;
- d. supply of nutrients;
- e. light (absence of turbidity);

Secondary parameters – releasing GHG stock

Parameters that modulate gas exchange between the atmosphere and the reservoir or downstream river:

- a. wind speed and direction;
- b. reservoir shape;
- c. rainfall;
- d. water current speeds;
- e. water temperatures;
- f. water depth and changes in water depth;
- g. reductions in hydrostatic pressure as water is released through low-level outlets;
- h. increased turbulence downstream of the dam associated with ancillary structures, e.g. spillways and weirs.

Most of these parameters and processes must be placed in a geographic and temporal context and need to be expressed on an areal basis. Therefore, accurate information is needed on the areal extent of the upland catchment and its land cover and land uses; the temporally varying areal extent of aquatic habitats in the reservoir and downstream river; and the bathymetry of the reservoir. Information is also required on the terrestrial carbon stocks present in the area before impoundment and on the net emissions of GHGs from the original ecosystem.

2.2.3. The importance of considering net emissions

Net GHG emissions from man-made freshwater reservoirs are defined here as the GHG impact from the creation of these reservoirs. As net GHG emissions cannot be measured directly, their value has to be estimated by assessing gross GHG emissions in the whole affected area, comparing the values for pre- and post-impoundment conditions.

This section presents the main concepts associated with the estimation of net GHG emissions from freshwater reservoirs. The detailed method for net GHG assessments is presented in the *Calculation Manual*; it describes how to calculate net emissions from the creation of a reservoir in a river basin. For each reservoir to be measured, it is

necessary to go through several steps in the data analysis, as is illustrated in Figure 1.1 (Section 1).

2.2.3.1. Definition of net emissions

To define the magnitude of GHG fluxes for a given reservoir, gross and net GHG emissions have to be assessed and calculated. According to Varfalvy (2005), gross emissions are those measured at the water-air surface, while net emissions are gross emissions minus pre-impoundment natural emissions (both terrestrial and aquatic ecosystems) at the whole-basin level, including upstream, downstream and estuarine. It is also necessary to account for emissions due to the above-water decay of trees killed in the reservoir, and where the water table is elevated along the shoreline, as well as emissions from concrete, steel, fuel, and others during the construction phase (even when they are not considered important for the reservoir's life cycle). However, emissions associated with land-use change (including deforestation, agricultural practices, and urbanisation) have to be approached with care, as they do not always directly result from the dam construction.

So, to quantify the net GHG emissions from a reservoir, emissions have to be studied before, during and after the reservoir's construction. The concept adopted here is that true net GHG emissions are obtained by the difference between pre- and post-reservoir emissions from the whole river basin. Because emissions from the construction phase also have to be considered, future editions of these *Guidelines* will include a method for doing so. The study period of emissions should be calculated as 100 years (UNFCCC; IPCC, 2006).

Data in the scientific literature are scarce on net GHG assessments from freshwater reservoirs. It is the intention of these *Guidelines* that this paucity of information is addressed, however it is anticipated that net will be significantly lower than the gross emissions.

The importance of reliable estimates of net GHG emissions from freshwater reservoirs underlines the need for pre- and post-impoundment assessments, including the role of carbon and nutrient loading from the catchment, from natural and unrelated human activities.

2.2.3.2. Measurement of gross emissions

Meteorological instruments are routinely used to measure and record wind speed and direction, air temperature, rainfall, and incoming solar radiation. For measurements within reservoirs, thermistors,

current meters, lagrangian GPS drifters and oxygen sensors are available. Concentrations of dissolved and particulate OM and nutrients are determined from laboratory analyses on samples collected from the reservoir, from inflow from the catchment and from the downstream river. Hydrological measurements of discharge and water depth are performed with current meters and pressure transducers or stage gauges (UNESCO/IHA, 2008).

Carbon loading occurs through internal inputs from the primary production of flooded soil and plant biomass, and through external loading from rivers, streams, and subsurface inflow. Measurement of primary productivity requires sequential biomass measurements of woody and herbaceous vegetation growing in the reservoir, and of uptake of dissolved inorganic carbon or evolution of oxygen by algae. The biomass of macrophytes growing in the reservoir is determined by direct sampling. Carbon included in the flooded soils and in the plant biomass can be measured directly or estimated using databases such as those at the Carbon Dioxide Information Analysis Center (CDIAC). External loads are the product of water discharge rate and the concentration of dissolved and particulate organic carbon (UNESCO/IHA, 2008).

CH₄ and CO₂ production rates during the mineralisation of these different pools of OM can be measured by incubation in anoxic conditions. In natural lake sediments, the degradation rates of OM and the resulting CO₂ and CH₄ benthic fluxes can be obtained by vertical profiles in sediment pore waters or from benthic chamber experiments. Sampling OM in the flooded and interstitial water can be difficult due to the presence of plant and tree material, precluding the use of box cores and benthic chambers. If this is so, an *in vitro* approach can be used. Samples of soils and vegetation similar to those that were flooded are retrieved from the river basin and are incubated with water in anoxic conditions. CO₂ and CH₄ potential production rates are then followed over time. Measurements of CO₂ production under aerobic conditions are also needed to estimate heterotrophic respiration in the epilimnion of the reservoir and in the river downstream of the dam (UNESCO/IHA, 2008).

In aquatic ecosystems, aerobic CH₄ oxidation is an important factor controlling CH₄ fluxes to the atmosphere. This process significantly affects the balance between CH₄ and CO₂ emissions. The extent of the process is determined by

the incubation of samples from the reservoir epilimnion and the river downstream (*UNESCO/IHA, 2008*).

2.2.3.3. Change in storage in the reservoir

Most reservoirs act as sediment traps, and by accumulating carbon in the sediments they can trap a significant amount of carbon. To derive a correct estimate of the amount of trapped carbon it must be recognised that part of the reservoir's trapped sediment may previously have been carried to the ocean and deposited in marine sediments. Sediments can also provide anoxic conditions leading to CH_4 production. The total flux of carbon between the reservoir sediments and the atmosphere through the water body must be assessed. If possible, these fluxes should be measured. They can also be calculated as the difference between measurements of carbon input and output. Such calculations must be done with careful attention to the primary production in the reservoir and internal carbon turnover, as this can contribute significantly to the understanding of sequestration in the sediments and of carbon output (*UNESCO/IHA, 2008*).

2.2.3.4. Output from the reservoir

According to *UNESCO/IHA (2008)*, diffusive CO_2 and CH_4 fluxes at the air-water interface of the reservoir, and the river below a reservoir outlet, can be determined using floating chambers. It can also be calculated based on the partial pressure gradient at the air-water interface and an exchange coefficient that depends on wind speed, water-current speed, rainfall, and temperature gradients at the air-water interface. CH_4 fluxes through the vegetation and CO_2 exchanges by plants can be measured with transparent or dark chambers. CH_4 bubble fluxes from the reservoir are determined using inverted funnels coupled to gas collectors initially filled with water. Bubble fluxes mainly occur in shallow parts of reservoirs where the hydrostatic pressure is not high enough to dissolve CH_4 in the interstitial water. Since ebullition is episodic, quantifying it accurately can be difficult. However, this can be overcome by using appropriate measurement methods. It is important to extend sampling over long periods (days, weeks) to quantify it accurately. The inverted-funnel method can provide good accuracy because bubble-carried fluxes physically depend on depth. The funnels collect only the gas carried by bubbles because of the difference between the gas concentration inside bubbles and those introduced through diffusion. Thereafter an

ensemble of funnels placed at the same depth can provide good sampling of random bubbles because of the enlargement of the collection area and subsequent integration of the samples.

Degassing downstream of the dam has been estimated as the difference between the gas concentration upstream and downstream of the reservoir outlet, multiplied by the outlet's discharge. The gas concentrations should be sampled from ports in the conduits leading to the outlets, if available. The surface and vertical profiles of CH_4 and CO_2 concentrations can be determined by the headspace method followed by gas chromatographic analysis (HS-GC: see sections 3.4.1.1.3 and 3.5.1).

In addition to downstream degassing of CO_2 and CH_4 , dissolved and particulate organic carbon and dissolved CO_2 and CH_4 are discharged through the dam and transported away by the river. This output has been calculated as the product of the water discharge rate and the concentration of dissolved gases and of particulate and dissolved OM. However, for this calculation, it is necessary to consider CO_2 and CH_4 emissions, CO_2 production through river respiration of the OM produced in the reservoir, and CH_4 oxidation to CO_2 , in relation to the pre-impoundment conditions. Doing so will properly quantify the atmospheric emissions through this pathway and the export of OM downstream of the reservoir.

2.2.3.5. Pre-impoundment measurements

This section provides guidance on the parameters that need to be considered and on when to measure or estimate the conditions of the catchment in the pre-impoundment state. The main concepts and equipment available for measuring these parameters are described in section 2.4. Detailed descriptions are also provided in section 3 (*Field Manual*).

- If the impoundment is already in place, literature or measurements at reference sites (or both) may be useful. When using reference sites, measurements should be made in the catchment at representative sites for all relevant land and water uses, with a sufficiently precise time resolution to reveal seasonal changes.
- Year-to-year variations should be covered by sampling over several years, and comparable locations should be used for pre- and post-impoundment measurements.

- The measurements should represent the whole catchment, including contributing land areas, the upstream river system and the reservoir's reach downstream.
- Measurements must cover seasonal variations in GHG status of reservoirs, including climate, rainfall, runoff, biomass production, biomass degradation, land-use operation or other important factors affecting the carbon and hydrological cycle.
- High-resolution topographic maps of the headwater catchments and aquatic systems are critical. All significant terrestrial and aquatic habitats should be mapped and their area and distribution recorded in a geographic information system (GIS). Aerial photography or satellite imagery, or both, should be used and the resulting maps validated by field observations. These data will serve as the basis for calculating GHG emissions and carbon budgets.
- This mapping and the definition of terrestrial and aquatic habitats (percentage of surface area cover) form the basis of the subsequent characterisation of these habitats in terms of GHG emissions and carbon budget. The sampling effort must consider the variation in regional climate (wet season, dry season, transition period, winter, summer) and the area covered by each type of habitat, with the number of samples reflecting the natural variability of the parameter measured and the technique used.
- In some reservoirs, emissions downstream of the outlet can be an important component of the annual budget. GHG emissions must be monitored carefully along the part of the river that will be downstream of the future outlet(s), to provide a clear reference state for this part of the river.
- GHG emissions on a given pre-impoundment site are ideally assessed in three steps:
 - Determine the spatial variability of parameters that are likely to influence GHG emissions, e.g., ecosystem type, the soil carbon (and nitrogen) content, and the soil moisture.
 - Determine GHG emissions in each vegetation type under a range of climatic conditions.
 - Extrapolate the experimentally measured fluxes to the scale of the area to be

impounded. Do this by using the parameterisation obtained in the different ecosystems and environmental conditions. If part of the studied area has not been sampled, parameterisations published in the literature may be used. The fluxes can be mapped at the scale of the studied area by coupling the parameterisations with the forcing parameters (ecosystem, temperature, soil moisture, and so forth) measured *in-situ* or deduced by remote sensing. The spatial scaling-up needs to take place in contrasting climate conditions, if applicable.

Finally, GHG emissions need to be converted to CO₂-equivalent emissions (see section 4.5.4.1).

2.2.3.5.1. Catchment/reservoir – terrestrial

Pre-impoundment inputs from the contributing areas should be determined before reservoir construction, but may be measured after the construction of a reservoir if the post-impoundment upstream catchment has not been changed from the pre-impoundment conditions.

Measurements of the following parameters are relevant:

- Carbon loading from the catchment:
 - OM concentrations and runoff;
 - litterfall that enters the flowing water;
 - sediment transport.
- Water-quality and physical parameters.

2.2.3.5.2. Catchment/reservoir – aquatic

The following elements should be addressed:

- Carbon storage in sediments
- GHG emissions
- Carbon transport (DOC, dissolved organic carbon (DIC), total organic carbon (TOC))
- OM concentrations and C/N, C/P and N/P ratios in particulate and dissolved material
- Physical parameters:
 - current speeds in rivers and streams;
 - surface temperatures;
 - stability of density stratification in the water;
 - water depth and changes in water depth;
 - residence time of water in the freshwater system.

2.2.3.5.3. Downstream of the reservoir site

The following elements should be addressed:

- Carbon transport (DOC, DIC, TOC)
- Carbon storage in sediments
- Physical parameters:
 - current speeds in rivers and streams;
 - surface temperatures;
 - water depth and changes in water depth.

2.2.3.5.4. Assessment of carbon stock

GHG production after impoundment is proportional to the amount of decomposable biomass stock. Thus, the evaluation of the carbon stock present in the area to be flooded by the reservoir is a critical measurement, along with carbon loading from the catchment.

Biomass and soil organic carbon (SOC)

Two types of biomass can be distinguished and both should be determined: the aboveground biomass (including living and dead biomass) and the belowground biomass (roots). The SOC includes both living organisms and detritus and should also be quantified. The maps of terrestrial habitats should be used to quantify the biomass and SOC.

Determining terrestrial biomass is time consuming. If no literature values are available, the aboveground biomass is assessed by taking samples from a known area of each type of vegetation and weighing each vegetation layer. Below-ground biomass is assessed by weighing all fine roots and estimating total roots using a root-to-shoot ratio. Wet biomass data are transformed into dry quantities and carbon content, and then extrapolated to the total inundated area.

SOC measurements can be made by sampling each soil type. Sampling cores should be 30 cm deep and divided in three strata. Chemical analysis is used to quantify organic carbon content. Soil density is also assessed. Additional analyses on N, P and Fe increase the level of information on soil chemistry.

Assessment of carbon transport in streams

POC, DOC and DIC should be measured at representative stages of the hydrographs of the streams. When coupled with discharge calculations, these measurements permit determination of carbon transport.

2.2.3.6. Post-impoundment measurements

This section provides guidance on the parameters that need to be considered after impoundment and on when to measure or to estimate the conditions of the catchment.

Measurements should be made in the catchment and the reservoir at representative sites with sufficient temporal resolution to cover seasonal changes. Except for measurements in the reservoir and for downstream degassing, post-impoundment measurements should be similar to pre-impoundment measurements (see previous section). The same locations should be used for pre- and post-impoundment measurements, whenever possible.

As with pre-impoundment, the measurements should be able to represent the whole catchment, including headwater areas, the river system and the reach downstream of the reservoir. Again, measurements must be made often enough to cover seasonal variations in GHG status of freshwater reservoirs, including climate, rainfall, runoff, biomass production, biomass degradation, nutrient loading, land-use operation or other important factors affecting the carbon and hydrological cycle.

2.2.3.6.1. Catchment

As for pre-impoundment conditions (both terrestrial and aquatic), carbon loading from the catchment and physical and water-quality parameters should be measured.

2.2.3.6.2. In the reservoir

The following elements should be addressed:

- carbon storage, including sediments and water column;
- GHG emissions;
- physical parameters that characterise hydrological and hydrodynamical conditions.

Special attention should be paid to the drawdown zone, where emissions may be higher due to re-growth of vegetation when water levels are low, leading to their decomposition after re-flooding.

2.2.3.6.3. Downstream of the reservoir site

The river system downstream of the planned (or existing) reservoir must be investigated to determine changes in carbon transport, carbon storage or GHG emissions between pre- and post-impoundment. Measurement sites should include all the outlets of the reservoir and the downstream river channel.

It is important to assess the change in nutrient delivery and primary productivity in the coastal zone, as changes in the water's nutrient content can reduce primary productivity (and carbon sequestration in sediments) in the estuary. Nutrient transport is an important element in the process. Its overall impact on the whole cycle needs further research.

2.2.4. Standardisation of units

In a modelling framework, amounts of chemical substances (for concentrations, fluxes, biogeochemical reaction rates, etc.) must be expressed in moles for stoichiometric calculations. Fluxes of CO₂ and CH₄ can be expressed in grams of carbon per square metre per day (g C m⁻² d⁻¹). All other measurements must be expressed using the International System of Units (SI).

2.3. Spatial and temporal resolution of sampling

This section describes how seasonal changes in climate, hydropower operations and carbon load may affect the spatial and temporal variations.

When designing a measurement campaign to capture the net GHG emissions from a reservoir in a river basin, it is important to analyse the potential spatial and temporal variability in possible GHG emissions. The analysis should take into account how seasonal changes in climate, reservoir operations and carbon load may affect temporal variability. Considerations of vegetation and land use (pre- and post-impoundment), hydrological and water-quality issues, and other anthropogenic activities should be included when designing the spatial sampling. Practical issues like accessibility, safety and other indirect implications must also be considered.

To accurately estimate a reservoir's atmospheric emissions, the seasonal variation of the fluxes by the whole reservoir system must be studied (including the reservoir, the degassing and the river downstream). As shown at the Petit Saut and Balbina reservoirs, atmospheric emissions vary by more than one order of magnitude within a year because of the seasonal variation in organic carbon supply, thermal stratification, irregular convective mixing, water depth, and reservoir operation. A monthly data set over ten years from the Petit Saut reservoir showed higher seasonal variations of gross emissions than the inter-annual variation. So estimates based on just one or two surveys a year should be read with caution.

Monthly monitoring of key parameters and CO₂ and CH₄ fluxes may be needed to cover the seasonal variability and provide robust mass balance measurements for the studied reservoirs. During these campaigns, measurements should span several days and include multiple sample series each day. The main goal must be to get reliable results that cover seasonal variations throughout the year. A careful analysis of the hydrology, including precipitation, temperature and the reservoir's past operation, could provide important information on the temporal resolution required. A case-by-case analysis of the environmental conditions of each reservoir may justify less frequent measurements (UNESCO/IHA, 2008).

The number of sampling stations is a compromise between budget, human resources and detailed objectives. The number of sampling points and the sampling frequency depend on the observed heterogeneity of the system and the desired resolution. Fixed sampling intervals are easier to analyse, but more frequent sampling during periods of greater variation allow more precision for the estimates of time-dependent variables.

More details in section 3 and section 4.

2.3.1. Where to measure

According to UNESCO/IHA (2008), the monitoring of reservoirs should be split to reflect the distinct regions and main processes in each of these regions. Different types of sampling stations may need to be chosen for long-term monitoring, i.e. stations:

- on the upstream reach, and other points of inflow;
- along the longitudinal axis of the reservoir;
- in vegetated and non-vegetated littoral zones of the reservoir;
- in embayments in the reservoir, where they exist;
- close to the reservoir outlets (normally close to the dam site, but varying from reservoir to reservoir) and from water passageways to understand the mixing of the water column in the reservoir;
- in the river downstream of the reservoir outlets.

Straskraba and Tundisi (1999) suggest two different sampling protocols: a simpler set of procedures for small reservoirs and a more comprehensive sampling for other types of reservoir. The simpler procedure includes only one sampling point in

the reservoir, with samples being collected at maximum stratification and during the period of complete homogenisation. This may however lead to significant uncertainty in the data obtained. The more comprehensive procedure includes sampling collections at the main upstream tributary, in the main reservoir body, and downstream. More sampling points are needed for bigger reservoirs, especially those with complex shapes and many tributaries. Sampling in the main body of the reservoir should occur at several depths at deeper locations, usually close to the dam. Reservoir depth plus thermal and chemical stratification will determine the number of sampling points (and spacing) in the water column. Samples systematically collected at the same depth are easier to analyse, but important extra information can be got by sampling water at depths where important changes are observed. Surface water should be sampled at 20 to 30 cm depth, to avoid influence from particles at the water surface. Bottom water should be sampled at 1 to 2m from the bottom of the reservoir. The depth-sampling interval should not be greater than 10m for stratified water bodies. The sampling frequency should be at least monthly (see section 4.3).

As sediments accumulate and integrate carbon storage over time, sediment samples do not need to be taken with a high temporal resolution. However, the spatial resolution of sediment samples needs to be more detailed. Carbon stock and carbon stock change in the sediments should be measured in different parts of the reservoir, covering the variation in pre-impoundment land-use/vegetation as well as circulation, inflow and deposition heterogeneities.

Section 3.2.3 discusses the criteria for defining the spatial resolution of sampling stations for both terrestrial and aquatic eco systems.

Recommendations

Depending on the reservoir's age, the site's complexity, and the resources available, a minimum and an optimum number of measurements are suggested:

- Minimum – At least, sufficient numbers to characterise: (1) the main inflow into the reservoir; (2) the emissions in the main reservoir body; (3) the conditions downstream of the reservoir outlet. Care should be taken around uncertainty in the data obtained as a result of the small number of stations (see section 3.2.2).
- Optimum – Determine spatial variability in detail during the first year using a large

number of stations to capture the reservoir's heterogeneity. The number depends on the reservoir's size and physical characteristics but must include its main inflow channel(s) and the sides or bays. In subsequent years, the number of stations can be reduced to a representative set capturing the main characteristics (see section 3.2.1 and Figure 3.2).

Emissions and concentrations must be studied along the river course until CO₂ and CH₄ partial pressures reach the natural background levels. The number of sampling stations will depend on the length of the river course affected by the dam.

When there is a low-level outlet, degassing should be followed downstream, with emissions studied along the river course, until CO₂ and CH₄ partial pressure reach the natural background levels. The number of sampling stations will depend on the length of the river course affected by the reservoir.

Measurements within outlet conduits (at relief valves for example) can reduce the need for measurements at inlets.

The drawdown zone can be an important source of emissions. Regular measurements should be made when the drawdown area is greater than a specified threshold (for example, 10% of the total flooded area).

Measuring at the spillway can be dangerous. Samples should be collected as close as possible to the sill and always above it.

2.3.2. When to measure

According to UNESCO/IHA (2008), the seasonal variation of the fluxes of the whole reservoir system (including the reservoir and the river downstream) must be studied to allow emissions from a reservoir to be accurately estimated. Emissions may vary by more than one order of magnitude in a year because of the seasonal variations of organic carbon supply, age, thermal stratification, irregular convective mixing, depth, and reservoir operation.

Recommendations

Temporal resolution

- The age of the reservoir is important. Younger reservoirs need more frequent measurements than mature reservoirs.
- At least a monthly monitoring of key parameters and GHG fluxes is likely to be required to cover the seasonal variability and provide robust mass balance measurements.

- Minimum – where seasonality is important, at least four measurement surveys per year are recommended: in the tropics, one in the dry season, one in the wet season, and the other two to capture the changes between them; in cold regions, two in winter (if ice-cover occurs, one before freezing and one after ice-breaking) and two in the summer.
- Optimum – automated systems to provide continuous measurements of CO₂, CH₄, water temperature and dissolved oxygen may provide the most useful information (*Demarty et al., 2009*).
- The short-term dynamics of GHG emissions can also be important in tropical reservoirs. Recent field studies at Manso Reservoir, in Brazil (*Assireu, 2009*), indicate that semidiurnal stratification processes mean there is merit in taking at least one measurement during the day and one at night in tropical reservoirs, especially during periods of reservoir stratification.
- Where possible, pre-impoundment conditions should also be monitored for at least one year.

Section 3.2.4 outlines the main criteria for defining the temporal resolution of sampling.

Duration

Previous research has shown significant inter-annual variation; therefore, at least two years are recommended for mature reservoirs. For new reservoirs, if high gross emissions are observed, longer periods (up to ten years) may be needed to account for emission reduction over the reservoir's lifetime (see section 4.3.1).

2.4. Methods and equipment

This section presents the main concepts in measuring GHG emissions, carbon mass flow (TOC, DOC, DIC, POC), carbon storage in sediments, and physical and water-quality parameters.

Descriptions of the (standardised) equipment and designs are presented in section 3.

2.4.1. Procedures for measuring GHG emissions

What to measure

The measurement should include all three GHG gases: CO₂, CH₄ and N₂O.

These gases are emitted from natural aquatic and terrestrial ecosystems, as well from anthropogenic sources.

According to UNESCO/IHA (2008), previous studies showed that the emissions of CO₂ and CH₄ may be relevant to global inventories of GHG exchanges.

CO₂ emissions are potentially similar at the basin level (pre- and post-impoundment), but may be influenced in time and space by a reservoir's creation. CO₂ is likely to account for more than 80% of a reservoir's GHG emissions.

CH₄ is the most important component to be evaluated, due to its high global-warming potential (21 to 25 times stronger than CO₂ over 100 years per molar unit). CH₄ emissions may also result from the conditions prevailing after the construction of a reservoir that were not present before. CH₄ emissions should be accounted for over the reservoir's life expectancy.

Not enough is known about N₂O emissions from freshwater reservoirs to predict its magnitude, although it can be significant in terrestrial systems. The few published studies report very low N₂O emissions in boreal ecosystems and there are no conclusive results for tropical reservoirs. A preliminary analysis of N₂O emissions from tropical reservoirs (*Guérin et al., 2008*) indicates that while gross N₂O emissions can be significant, net emissions are expected to be considerably lower. N₂O emissions can usually be measured at low extra cost and these measurements are recommended until more becomes known.

How to measure

These comments and recommendations apply to both pre- and post-impoundment conditions.

In the case of pre-impoundment conditions, both terrestrial and aquatic systems can be present, and the use of literature data and reference sites is suggested when measurements are unavailable. Future editions of these *Guidelines* should include a review of relevant literature sources for emission rates from different vegetation types.

As a rule, measurements should be taken at the same reference points for both pre- and post-impoundment studies.

The following items describe the main concepts related to the suggested equipment and procedures to be used for estimating GHG emissions for terrestrial systems, surface flux, bubbling and downstream emissions. Detailed descriptions of the equipment and its use are provided in sections 3.3 (terrestrial systems) and 3.4 (aquatic systems).

2.4.1.1. Terrestrial systems

The most commonly used pieces of equipment for estimating GHG emissions in terrestrial systems are chambers, soil core incubators and eddy covariance towers, as described below.

a. Chambers

Chambers are commonly used to measure the emission of many trace gases from soil. The method involves placing an open-bottom chamber over a small area of soil surface and measuring the gas emitted into the chamber. The trapping arrangement may be by passive (static, closed) systems or active (dynamic, flowing) systems.

At the air-soil interface, GHG fluxes are measured using a static chamber equipped with a butyl rubber stopper that allows gas sampling with a syringe and needle followed by gas chromatography analysis. If the gas is analysed with an IRGA, the chamber has two openings. The chamber is installed on a collar inserted into the soil or the sediment at least one hour before measurement (but longer times should generally be allowed due to root damage at insertion). The sealing of the chamber on the frame is ensured by a slot filled with water.

The advantages regarding chambers include:

- simplicity and ease in fabrication and operation;
- the large effect on the within-chamber environment created by the static chambers may be reduced by appropriately designed and operated dynamic chambers;
- appropriate design and use can minimise the bias of underestimation or overestimation of the actual flux.

The constraints regarding chambers include:

- when the chamber sampling area is a small fraction of the total emitting area, the measured flux could be highly variable due to soil spatial heterogeneity;
- the presence of the chamber can change the environmental properties (such as soil temperature and the wind profile near the soil surface) of the sampled area;
- the air flowing through the dynamic chamber may change the pressure gradient between the soil-gas phase and the chamber interior;

- micro climate (temperature, humidity, and pressure) inside the chamber may be different from the natural surrounding environment.

See section 3.3.1.2.1 for more detail.

b. Incubators (soil core sampling)

Soil emissions can be estimated by the soil incubation method. Two variants of the method can be used: air incubation, which estimates emissions in terrestrial environments, or water incubation, which estimates emissions in flooded environments.

The incubation method is used to estimate GHG emissions from specific soil types under predefined conditions. Soil samples are collected from the study area and taken to the laboratory, where they are prepared according to the type of incubation to be performed, and then placed in incubators under controlled temperature or moisture conditions (or both). Temperature-controlled rooms or incubators are necessary for this test. GHG emissions are measured by putting the incubated soil sample in a sealed container from which air samples are drawn over a given period of time. Samples are analyzed on a gas chromatograph for CO₂, CH₄ and N₂O concentration, and flux is calculated as the change in concentration over time.

The advantages regarding incubation of soil cores include:

- less expensive;
- allows collection of data with good spatial resolution.

The constraints regarding incubation of soil cores include:

- homogenisation and incubation processes can affect emission rates;
- field calibration may be necessary.

Incubation of soil cores can be an adequate method for studying processes occurring in the soils or sediments (potential production or oxidation). However, this approach cannot be used for determining fluxes.

Inclusion of soil core incubation measurements is promising but the method needs to be studied further and compared to more intensive monitoring. See section 3.3.1.1 for further detail.

c. Eddy covariance towers

The eddy covariance technique measures vertical fluxes within turbulent atmospheric boundary layers. Tower-mounted instruments measure the vertical wind and the concentrations of gas many times per second. From the product of these it is possible to calculate the net flux of the gas between the atmosphere and an area upwind of the tower.

The advantages regarding eddy covariance towers include:

- extensively used;
- well-tested for terrestrial systems;
- continuous data over long periods;
- large spatial coverage (several hectares);
- footprints can be separated on the basis of wind direction and speed.

The constraints regarding eddy covariance towers include:

- very expensive (but this must be considered in relation to the manpower needed for other data collection systems): high towers may be needed over land and stable platforms are needed over water (high towers are not needed over water but it is best to have a stable platform, a fixed rig rather than a buoy);
- the data processing is mathematically complex, and requires significant care;
- intense data interpretation is necessary;
- less developed and tested over water (although it has been used over lakes successfully);
- gap filling often needed to obtain annual seasonal budgets;
- wind direction dependent;
- require large homogeneous footprint, although this depends on the scale of heterogeneity. This requirement can be an advantage if small-scale heterogeneity needs to be integrated.

See section 3.3.1.3.2 for more detail.

Alternative ways to estimate emissions

- Land-use maps and satellite images combined with literature data.
- Literature data must be used for canopy calculations of emission rates.

Recommendation: Use literature data and reference sites when measurements are unavailable. A future revision of these *Guidelines*

will include a review of literature sources for emission rates from different vegetation types.

2.4.1.2. Aquatic systems**2.4.1.2.1. Diffusive surface flux between water and the atmosphere**

The source of carbon for the CO₂ and CH₄ is derived from:

- OM imported from the catchment;
- OM produced in the reservoir;
- decomposition of OM in plants and soils flooded by the reservoir.

Diffusive CO₂ and CH₄ fluxes at the reservoir's air-water interface can be determined using floating chambers or eddy covariance towers. In the river downstream, floating chambers can be used. Alternatively, fluxes can be calculated based on the partial pressure gradient at the air-water interface and an exchange coefficient that depends on wind speed, water current velocity, rainfall, and temperature gradients at the air-water interface, as used in the thin boundary layer (TBL) diffusive process model.

a. Surface floating chambers

The floating chamber method is a cheap and convenient method of measuring direct diffusive fluxes at the surface of aquatic ecosystems. This method consists of enclosing air in a chamber that floats at the water surface. Fluxes are then calculated according to the change of the concentration of the gas in the chamber (*e.g. Abril et al. 2005, Guérin et al. 2007, Tremblay and Bastien 2009*).

Good use of a floating chamber

As discussed by Kremer et al. (2003b), a chamber that moves relative to the surface water would disrupt the aqueous boundary layer and artificially enhance gas exchange. If fluxes are not measured while floating freely with water movements, this leads to a significant overestimation of the fluxes, since turbulence is artificially enhanced by the friction between the chamber walls and the water. Thus, measurements must be performed while the chamber drifts with the water at lake and river surfaces. In environments with low water currents, but high wind, it is preferable to anchor the chamber to avoid its moving in the wind, but in environments with high currents, the chamber needs to drift with the water mass (*Frankignoulle et al., 1996*).

The advantages of surface floating chambers include:

- inexpensive and can be transported and deployed rapidly;
- easy and precise measurements;
- can be connected to real-time measurement systems.

The constraints of surface floating chambers include:

- provide only a point measurement in space and time;
- in the presence of currents, all measurements have to be made while the chamber is drifting with the water. Measurements on a drifting boat can be difficult on rapid waters (rocky, fast and diverse sites), so that exaggerated results arise when there is a water current under a fixed chamber;
- no standard design;
- effect of wind speed on measured fluxes.

See section 3.4.1.1.1 for further detail.

b. Eddy covariance towers

This method is already described under section 2.4.1.1, as it has been most widely used for terrestrial systems.

The technique is good, but current land-based instruments probably need to be sturdier for use in water. It can be used to compensate for shortcomings in other areas and will give more value if there are sufficient financial resources and an adequate area available.

See section 3.4.1.1.2 for more details.

c. Thin boundary layer (TBL) diffusive process model

The TBL method calculates flux using semi-empirical equations. Plenty of literature exists on this subject, yet the mechanisms that drive the process remain poorly understood so predictions have large uncertainty. For example, widely used predictive models of the gas transfer process commonly differ by factors of three or more, and contain poorly understood non-linearities, as noted by Banerjee and MacIntyre (2004). This translates to uncertainties of at least 300% in recent attempts to calculate a net oceanic CO₂ uptake (Takahashi *et al.*, 2002). Such uncertainty arises from the highly variable nature of correlating factors, e.g., wind, waves, surfactants, thermal convection or stratification, wave breaking, and upwelling. The local parameters necessary for

the calculations are the concentration of the GHG in air and in the water, the wind speed and the water temperature.

The advantages with regard to TBL include:

- very quick method: a site can be sampled in less than five minutes;
- samples can be kept for months, when positioned and stored in correct conditions (in the dark and bottom up so the gas phase only has contact with the glass);
- unstable water samples have to be analysed rapidly;
- can be converted into gas concentrations using solubility equations (for CH₄ and CO₂) and pH (for CO₂);
- time series are easy to obtain.

The constraints with regard to TBL include:

- relationships are site-specific;
- theoretical equations are not validated at low and high wind speeds.

See section 3.4.1.1.3 for further detail.

Recommendation: Use floating chambers connected to a real-time measurement system (if wind and weather conditions allow). This system should be used in both pre- and post-impoundment studies. If real-time measurements are not feasible, do measurement campaigns with floating chambers in accordance with spatial and temporal resolution requirements. In future, TBL might be used more often, but the approach still needs to be tested more.

2.4.1.2.2. Bubbling (or ebullition)

The gases generated in the reservoir sediment are initially dissolved in the interstitial water. The less soluble gases, such as CH₄, aggregate as bubbles that can grow until they are liberated and migrate to the water surface. At deeper depths, bubbles dissolve in the water on their way to the atmosphere. Also, shallow waters with high oxygen concentration can be a CH₄ sink, as the bacteria in these waters can oxidise CH₄ to CO₂.

Bubble fluxes mainly occur in shallow parts of reservoirs where the hydrostatic pressure is not sufficiently high to dissolve CH₄ in the interstitial water. Because ebullition is intermittent it is important to extend the collection time over several days. This process can be important in regions where peatland is impounded, as ebullition is known to be an important pathway for CH₄ emission in many peatlands (Christensen

et al., 2003). It can be important in warm and shallow water with OM, but it is more likely to occur in waters up to 10m depth (Although bubbling has been identified at depths of over 10m). This implies that the bathymetry of the reservoir has to be considered when extrapolating the measurements, as mainly shallow zones need to be included.

In the drawdown zone of the reservoir, because water-level fluctuation, coupled with wave action, results in the organic sediments being eroded and reduces OM availability, bubbling is important only if the surrounding terrestrial areas provide sufficient amounts of OM.

Bubble collectors installed below wind-wave influence can be used to integrate bubble emission over time and are cheap and easy to operate. The ebullition can therefore be integrated over the whole season. Open floating dynamic chambers have been used to measure bubble emission (Ramos *et al.*, 2006). Acoustic techniques have also been used to quantify bubbles (Ostrovsky, 2003; McGinnis *et al.*, 2006; Ostrovsky *et al.*, 2008).

In the most used method for measuring bubbling, the ascending bubbles are captured by inverted funnels coupled to gas collectors initially filled with water.

Samples are collected using a set of funnel collectors. If the environment is believed to emit small amounts of bubbles, large bubble collectors

should be installed for longer periods to collect as many bubbles as possible.

In most cases, the funnels are placed along transects from the shallows to the deepest regions. Spatial resolution must be decided on the basis of reservoir size and bathymetry and soil/sediment composition.

The funnels are submersed and all air is removed to avoid contamination by atmospheric air. Then the collecting bottles, full of water, are coupled to the funnel.

The choice of the sampling site and the arrangement of funnels are determined by parameters such as the density of the flooded vegetation, the number of years since the reservoir was filled, depth, presence of semisubmersed vegetation, and the geographic region of the reservoir.

The collection period can extend from 24 hours to several days, weeks or the whole season.

Samples can be collected in between and the volume in the collector can be recorded. The collection bottles are hermetically sealed while still underwater and are collected for later laboratory analysis. See section 3.4.1.2. for further detail.

2.4.1.2.3. Downstream emissions

Downstream emissions are those observed after the reservoir outlets (turbines, spillways, low-level outlets, etc.). They are composed of degassing and

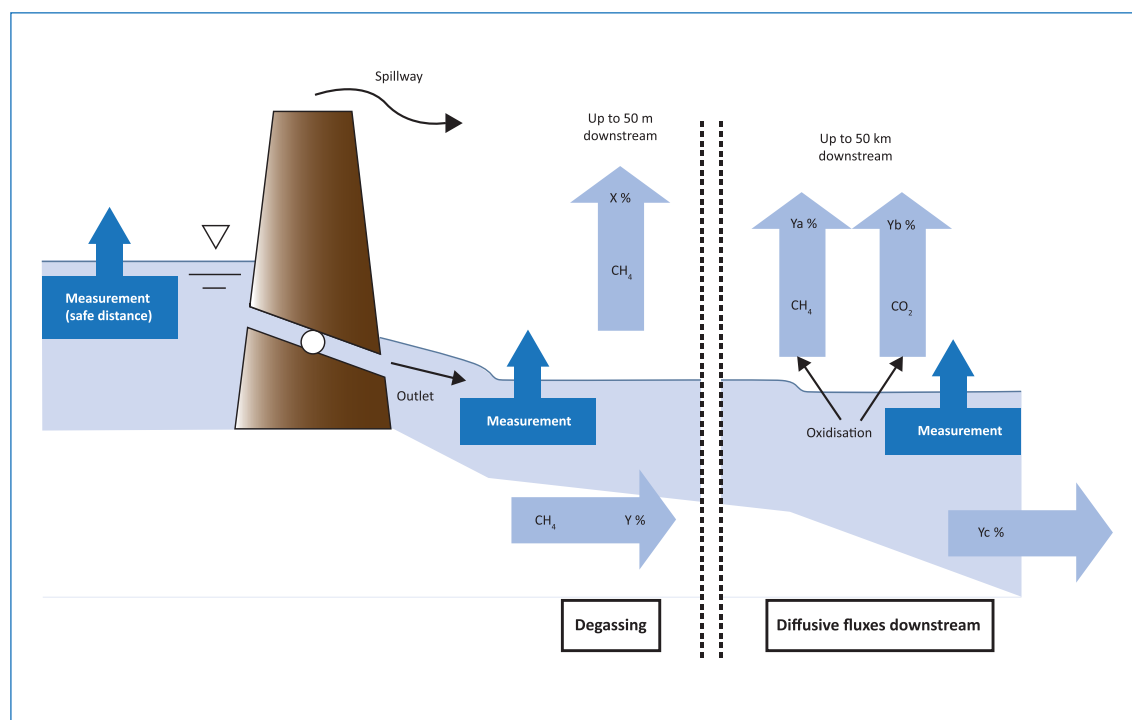


Figure 2.4: Schematics of downstream GHG emission patterns and suggested measurement points

diffusive fluxes, and their influence can range from a few tens of metres up to 50 km downstream of the dam. Studies show that there can be important emission rates close to the outlets, and these reduce gradually as the distance from the dam increases. The effects of the reservoir-induced emissions of CH₄ have been identified at 40 km (Petit Saut) and 30 km (Balbina) in the downstream river.

Figure 2.4 presents the schematics of downstream GHG emission patterns and suggested measurement points.

a. Degassing

Degassing is defined as an emission that happens on discharge from low-level outlets, including turbine tailwater, induced by dramatic pressure change. A wide variation in the importance of degassing has been reported (1% to 90% of total emissions), and its magnitude is influenced by dam design.

Degassing of water passing through spillways and turbines has been estimated on the basis of supersaturation of gases in the reservoir water body and its equilibrium concentration. (*IPCC GPG for LULUCF 2003*).

Degassing downstream of the dam has been estimated as the difference between the gas concentration upstream and downstream of the power plant multiplied by the outlet discharge. If possible, the gas concentrations should be sampled from ports in the conduits leading to the outlets. The surface and the vertical profiles of CH₄ and CO₂ concentrations can be determined by the headspace method followed by gas chromatographic analysis.

To accurately determine the degassing, samples representing water entering the turbines have to be taken directly in the turbines or at the entrance of the inlet to the powerhouse. When this is not possible, the degassing could be evaluated from the average GHG concentration calculated from vertical profiles of concentration in the reservoir. The concentration in spilled water must be determined from samples of water discharged by the spillway. The concentration of gas in water being discharged through the dam is the average of the concentration in water entering the spillway and the turbines weighted by the discharge of each water pathway. Downstream water samples must be taken away from the zone of turbulence just downstream of the dam. See section 3.4.1.3.1 for more detail.

b. Downstream diffusive fluxes

In addition to downstream degassing of CO₂ and CH₄, dissolved and particulate organic carbon and dissolved CO₂ and CH₄ are discharged through the dam and transported downstream. This output has been calculated as the product of the water discharge rate and the concentration of dissolved gases, DOC and POC. However, to properly quantify the atmospheric emissions through this pathway and the export of OM downstream of the dam it is necessary to include calculations of:

- the out-gassing of CO₂ and CH₄;
- the production of CO₂ by the respiration in the river of the OM produced in the reservoir;
- the oxidation of CH₄ to CO₂.

The presence of currents and rapidly flowing water can make it difficult and dangerous to measure these fluxes. These factors have to be taken into account when planning measurement campaigns. In most cases, the best available method for calculating downstream diffusive fluxes is through an equation of gas concentrations, getting the data at the appropriate depths in the water above and below the dam.

It is also important to take into account flux contributions from the catchment in the downstream section (tributaries, direct runoff).

Recommendations

- Measurements should be taken at the entry point of the outlet (spillway, turbine, low-level outlet).
- Measurements should be made in conduits whenever possible (or as close as possible to the intake), with a concentration measurement downstream of the dam. A specific sampling technique will need to be designed for each individual outlet.
- Spillway emission has to be included.
- Diffusive fluxes and carbon transport from rivers below dams or at the outlet of the powerhouse have to be measured. The fast-flowing water is likely to make floating chambers inaccurate, but concentration measurements can be used instead, as described in section 2.2.3.4
- A simple and conservative approach would be to measure GHG concentrations at the spillway intake or in the conduit and at an appropriate distance downstream where dissolved gas

levels can be assumed to have returned to natural levels. In this method, the difference in measured values can be considered as the downstream emissions.

2.4.1.2.4. CO_2 , CH_4 and N_2O concentrations

Gas chromatography (GC) can be used to analyse dissolved gas in water, using the headspace techniques. For CO_2 , CH_4 and N_2O concentrations, surface water is sampled with a custom sampler that limits gas exchange, such as the one designed by Abril et al. (2007).

Gas concentrations in the water are calculated from partial pressures in the headspace, using the solubilities given by Weiss (1974) for CO_2 , Yamamoto et al. (1976) for CH_4 and Wanninkhof (1992) for N_2O . For CO_2 , as described by Hope et al. (1995), this method is the most appropriate for acid, low-ionic-strength, organic-rich waters, as at PSR, Balbina and Samuel Reservoirs. See sections 3.4.1.1.3 and 3.5.1 for further information.

Infrared gas analysers can also be used for measurements in both terrestrial and aquatic systems. See section 3.5.2 for further information.

As release of gases from the storage of dissolved gas in the water body is one of the pathways of GHG emission (Bastviken et al., 2004) it is important to keep track of that storage. The size of the storage can be affected by upwelling in a stratified reservoir (Effler et al., 2004). High wind speed can also cause degassing of the water body. As floating chambers cannot be operated in high wind speed conditions, diffusive fluxes are underestimated during these degassing events. Regular measurements of gas concentration profiles in reservoirs could therefore be an important contribution towards measurements of diffusive emission, especially in windy conditions.

2.4.2. Carbon mass flow and carbon storage in sediments

What to measure

Carbon can be in particulate or dissolved form, and part of the dissolved carbon can be in the form of mostly bicarbonate ion. Dissolved organic components are, in part, humic and fulvic acids, although other forms, such as urea and sugars, can also be present (Matvienko, 200-). The forms to be measured are:

- total organic carbon (TOC);
- dissolved organic carbon (DOC);

- dissolved inorganic carbon (DIC);
- particulate organic carbon (POC).

Carbon loss to sediments should also be evaluated.

How to measure

The detailed methods for measurement and analysis of TOC, DOC, DIC and POC are described in USEPA (1997; 2001), APHA (1998), Matvienko (2000), and other sources.

Total organic carbon (TOC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) can be estimated by microanalytical methods using infrared spectrometry.

Particulate organic carbon (POC) can be quantified using a POC analyser that combusts the sample and determines the CO_2 . Inorganic carbon must be removed by acid treatment prior to this procedure.

The storage of OM in reservoir sediments is very difficult to quantify and as yet there is no satisfactory method to deal with this term, even though it may be significant in systems with naturally turbid waters or in eutrophic systems with high algal biomass.

Sediments in reservoirs are a mixture of post-impoundment settled material and the pre-impoundment soil. Sediments in reservoirs generally show a lot of patchiness and spatial heterogeneity, and the presence of dead trees increases the mesoscale (metric) heterogeneity and usually restricts the use of classical box corers. A single sediment core is never representative of an entire reservoir with a large surface area. Furthermore, sedimentation rates cannot be quantified using classical methods.

In principle, indirect estimation of organic carbon sedimentation and storage in reservoirs should be preferred. However, accumulated data from studies show that sedimentation traps already provide estimates of permanent carbon sedimentation. Data from Brazil and Finland show that of the fresh carbon settling daily, 89% is cycled back to the water column as CO_2 , CH_4 and potentially labile DOC. In tropical reservoirs, sediments are acidic and silica can be used as a tracer for permanent carbon sedimentation. According to field measurements, tropical reservoirs bury 9.3 times more carbon than they emit as CH_4 . Further, the permanent carbon sedimentation rate in tropical reservoirs is 268 million times greater than the carbon storage in tropical soils (Sikar et al., 2009).

2.4.3. Water quality and physical parameters

The main parameters to be estimated are:

- air temperature;
- water temperature;
- soil temperature;
- water pH;
- dissolved oxygen in water;
- water depth;
- wind speed;
- wind direction;
- mean annual rainfall;
- residence time;
- current speeds in rivers and streams;
- concentration of OM;
- concentration of nitrogen;
- concentration of phosphorus;
- concentration of iron;
- conductivity.

It is recommended that well-established water quality standards and criteria are used, such as those described by ISO (*ISO 5667-1:2006, ISO 5667-3:2003, ISO 5667-4:1987, ISO 5667-6:2005, ISO 5667-12:1995, ISO 5667-14:1998, ISO 5667-16:1998, ISO 5667-17:2008, ISO 5667-20:2008*), EPA-Queensland, Australia, ABNT 9897 (Brazil), USEPA, DEFRA-UK, CONAMA-Brazil, and other international, national and local standards.

2.5. References

- ABNT 9897. 1987. Planejamento de amostragem de efluentes líquidos e corpos receptores. NBR.9897. Rio de Janeiro: ABNT.
- Abril, G., Commarieu, M.V., and Guérin, F. 2007. Enhanced methane oxidation in an estuarine turbidity maximum, *Limnology and Oceanography*, 52(1): 470–475.
- Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Santos, M. A., and Matvienko, B. 2005. Carbon dioxide and methane emissions and the carbon budget of a 10-years old tropical reservoir (Petit-Saut, French Guiana). *Global Biogeochem. Cycles* 19: GB 4007, doi:10.1029/2005GB002457.
- APHA 1998. Standard methods for the examination of water and waste water. 20 ed. Washington: APHA.
- Assireu, A. 2009. Personal communication.
- Banerjee, S., and MacIntyre, S. 2004. The air-water interface: Turbulence and scalar exchange, in *Advances in Coastal and Ocean Engineering*, edited by P. L. F. Liu, pp. 181–237, World Sci., Hackensack, N. J.
- Bastviken, D., Cole, J., Pace, M., and Tranvik, L. 2004. Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Glob. Biogeochem. Cycle*, 18, Gb4009. doi: 10.1029/2004GB002238.
- Bridgman S.D., Updegraff K., and Pastor J. 2001. A Comparison of Nutrient Availability Indices Along Ombrotrophic- Minerotrophic Gradient in Minnesota Wetlands. *Soil Sci Soc Am J* 65: 259–269.
- Casper, P., Maberly, S.C., Hall, G.H. and Finlay, P.J. 2000. Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. *Biogeochemistry* 49: 1–19.
- Christensen, T. R., Panikov, N., Mastepanov, M., Joabsson, A., Stewart, A., Oquist, M., Sommerkorn, M., Reynaud, S., and Svensson, B. 2003. Biotic controls on CO₂ and CH₄ exchange in wetlands – a closed environment study, *Biogeochemistry*, 64: 337–354.
- Clein J.S., McGuire A.D., Zhang X., Kicklighter DW, Melillo JM, Wofsy S.C., Jarvis P.G., Massheder J.M. 2002. Historical and Projected Carbon Balance of Mature Black Spruce Ecosystems across North America: The Role of Carbon-Nitrogen Interactions. *Plant and Soil* 242: 15–32.
- Cole, J.J. and Caraco, N.F. 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. *Mar. Freshwater Res.* 52: 101–110.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.R., Duarte, C.M., Kortelainen, P., Downing, J.A., Middleburg, J. and Melack, J.M. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems* doi: 10. 1007/s10021-006-9013-8.
- Conrad, R. 1989. Control of methane production in terrestrial ecosystems. Pages 39–58. In M.O. Andrea and D.S. Schimel (eds.) *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. J.Wiley & Sons.
- Demarty, M, J. Bastien, Tremblay, A. and Gill, R. 2009. Use of automated systems to measure greenhouse gas emissions from boreal reservoirs in Manitoba and Québec, Canada. *Submitted to Environmental Science and Technology*.
- Delmas R., Galy-Lacaux, C. and Richard, S. 2001. Emissions of greenhouse gases from the tropical hydroelectric reservoir of Petit Saut (French Guiana) compared with emissions from thermal alternatives. *Global Biogeochem. Cycles*, 15: 993–1003.
- Duchemin, E., Lucotte, M., Camuel, R. and Chamberland, A. 1995. Production of the greenhouse gases CH₄ and CO₂ by hydroelectric reservoirs in the boreal region, *Global Biogeochem. Cycles* 9: 529–540.
- Dueck, T.A., de Visser, R., Poorter, H. Persijn, S., Gorissen, A. de Visser, W., Schapendonk, A., Verhagen, J., Snel, J., Harren, F.J.M., Ngai, A.K.Y., Verstappen, F., Bouwmeester, H., Voesenek, L.A.C.J. and van der Werf, A. 2007. No evidence for substantial aerobic methane emission by terrestrial plants: A 13C-labelling approach. *New Phytol.* 75: 29–35.
- Effler, S. W., Wagner, B. A., O'Donnell, S. M., Matthews, D. A., O'Donnell, D. M., Gelda, R. K., Matthews, C. M., and Cowen, E. A. 2004. An upwelling event at Onondaga Lake, NY: characterization, impact and recurrence, *Hydrobiologia*, 511: 185–199.
- EPA-Queensland, Australia. 1994. Water quality sampling manual: for use in testing for compliance with the Environmental Protection Act 1994.
- Frankignoulle, M., Bourge, I. and Wollast, R. 1996. Atmospheric CO₂ fluxes in a highly polluted estuary (The Scheldt). *Limnol. Oceanogr.*, 41: 365–369.

- Galy-Lacaux, C., Delmas, R., Jambert, C., Dumestre, J. F., Labroue, L., Richard, S., and Gosse, P. 1997. Gaseous emissions and oxygen consumption in hydroelectric dams: A case study in French Guiana. *Global Biogeochem. Cycles* 11: 47–483.
- Galy-Lacaux, C., Delmas, R., Kouadio, G., Richard, S. and Gosse, P. 1999. Long term greenhouse gas emission from a hydroelectric reservoir in tropical forest regions. *Global Biogeochem. Cycles* 13: 503–517.
- Guérin, F., Abril, G., Richard, S., Burban, B., Reynouard, C., Seyler, P. and Delmas, R. 2006. Methane and carbon dioxide emissions from tropical reservoirs: significance of downstream rivers. *Geophys. Res. Lett.*, 33: L21407, doi:10.1029/2006GL027929.
- Guérin F., Abril, G., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A. and Varfalvy, L. 2007. Gas transfer velocities of CO₂ and CH₄ in a tropical reservoir and its river downstream, *J. Mar. Syst.* 66: 161–172.
- Guérin F., Abril G., Tremblay A. and Delmas R. 2008. Nitrous oxide emissions from tropical hydroelectric reservoirs. *Geophysical Research Letters* 35, doi:10.1029/2007GL033057.
- Hahn M., Gartner K., Zechmeister-Boltenstern S. 2000. Greenhouse Gas Emissions (N₂O, CO₂, CH₄) from Three Different Soils Near Vienna (Austria) with Different Water and Nitrogen Regimes. *Die Bodenkultur* 51(2): 115–125.
- Hendzel, L.L., Matthews, C.J.D., Venkiteswaran, J.J., St. Louis, V.L., Burton, D., Joyce E.M. and Bodaly, R.A. 2005. Nitrous oxide fluxes in three experimental boreal forest reservoirs. *Environmental science & technology*, vol. 39, no12, pp. 4353–4360 [8 page(s) ISSN 0013-936X.
- Houweling, S., Röckmann, T., Aben, I., Keppler, F., Krol, M., Meirink, J., Dlugokencky, E. and Frankenberg, C. 2006. Atmospheric constraints on global emissions of methane from plants. *Geophys. Res. Lett.* 33: doi: 10. 1029/2006GL026 162.
- Huttunen, J.T., Väisänen, T.S., Heikkikinen, M., Hellsten, S., Nykänen, H., Nenonen, O. and Martikainen, P.J. 2002. Fluxes of CH₄, CO₂, and N₂O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland. *Global Biogeochem. Cycle.* 16: 1–17.
- Intergovernmental Panel on Climate Change (IPCC). 1990. First Assessment Report, Climate Change, Cambridge.
- Intergovernmental Panel on Climate Change (IPCC). 2001. Third Assessment Report, Climate Change 2001. Houghton J.T., Ding Y., Griggs D.J., Noguer M., Van der Linden P.J., Dai X., Maskell K., Johnson C.A., Published by IGES, Japan.
- Intergovernmental Panel on Climate Change (IPCC). 2003. Good Practice Guidance for Land Use, Land Use Change and Forestry. Punman J., Geytarsky M., Hiraishi T., Krug T., Kruger D., Pipatti R., Buendia L., Miwa K., Ngara T., Tanabe K., Wagner F. (eds). Published by IGES, Japan.
- Intergovernmental Panel on Climate Change (IPCC). 2006. IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme. Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published by IGES, Japan.
- ISO 5667-1:2006 2006. Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques.
- ISO 5667-3:2003 2006. Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples.
- ISO 5667-4:1987 1987. Water quality – Sampling – Part 4: Guidance on sampling from lakes, natural and man-made.
- ISO 5667-6:2005 2005. Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams.
- ISO 5667-12:1995 1995. Water quality – Sampling – Part 12: Guidance on sampling of bottom sediments.
- ISO 5667-14:1998 1998. Water quality – Sampling – Part 14: Guidance on quality assurance of environmental water sampling and handling.
- ISO 5667-16:1998 1998. Water quality – Sampling – Part 16: Guidance on biotesting of samples.
- ISO 5667-17:2008 2008. Water quality – Sampling – Part 17: Guidance on sampling of bulk suspended solids.
- ISO 5667-20:2008 2008. Water quality – Sampling – Part 20: Guidance on the use of sampling data for decision making – Compliance with thresholds and classification systems.
- Keller M. and Stallard R.F. 1994. Methane emissions by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research* 99: 8307–8319.
- Kelly C.A., Rudd, J.W., Bodaly, R. A., Roulet, N. P., St.Louis, V. L., Heyes, A., Moore, T. R., Schiff, S., Aravena, R., Scott, K. J., Dyck, B., Harris, R., Warner,

- B. and Edwards, G. 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. *Env. Sci. Technol.* 31: 1334–1344.
- Kemenes, A., Forsberg, B.R. and Melack, J.M. 2007. Methane release below a tropical hydroelectric dam. *Geophys. Res. Lett.* 34: L12809, doi:10.1029/2007GL029479.
- Keppler, F., Hamilton, J.T.G., Brass, M. and Röckmann, T. 2006. Methane emissions from terrestrial plants under aerobic conditions. *Nature* 439: 187–191.
- Kirschbaum, M.U.F., Bruhn, D., Etheridge, D.M., Evans, J.R., Farquhar, G.D., Gifford, R.M., Paul, K.I. and Winters, A.J. 2006. A comment on the quantitative significance of aerobic methane release by plants. *Funct. Plant Biol.* 33: 52 1–530.
- Kremer, J. N., Nixon, S. W., Buckley, B., Roques, P. 2003. Technical note: Conditions for using the floating chamber method to estimate air-water gas exchange. *Estuaries* 26: 985–990.
- Matvienko, B. 2004. The carbon cycle in hydroelectric reservoirs and the greenhouse effect. In: Rosa, L.P., Santos, M.A., Tundisi, J.G. 2004. Greenhouse gas emissions from hydropower reservoirs and water quality. Rio de Janeiro: COPPE/UF RJ, Brazil, 136 p.
- McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E., and Wuest, A. 2006. Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere? *Journal of Geophysical Research*, Vol. 111, C09007.
- Mengis M., Gächter R., Wehrli B. 1997. Sources and Sinks of Nitrous Oxide (N₂O) in Deep Lakes. *Biochemistry* 38: 281–301.
- Ostrovsky, I. 2003. Methane bubbles in lake Kinneret: quantification and temporal and spatial heterogeneity. *Limnology and Oceanography*, vol. 48, N.3.
- Ostrovsky, I., McGinnis, D. F., Lapidus, L., and Eckert, W. 2008. Quantifying gas ebullition with echosounder: the role of methane transport by bubbles in a medium-sized lake. *Limnol. Oceanogr.: Methods* 6: 105–118.
- Ramos, F. M., Lima, I. B. T., Rosa, R. R., Mazzi, E. A., Carvalho, J. C., Rasera, M., Ometto, J., Assireu, A. T. and Stech, J. L. 2006. Extreme event dynamics in methane ebullition fluxes from tropical reservoirs. *Geophysical Research Letters* 33(21). DOI: 10.1029/2006GL027943.
- Regina K., Nykänen H., Silvola J., Martikainen P.J., 1996. Fluxes of Nitrous Oxide from Boreal Peatlands as Affected by Peatland Type, Water Table Level and Nitrification Capacity. *Biogeochemistry* 35: 401–418.
- Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M. and Hess, L.L. 2002. Outgassing from Amazonian rivers and wetland as a large tropical source of atmospheric CO₂. *Nature* 416: 617–620.
- Rosa, L.P. and Schaeffer, R. 1994. Greenhouse gas emissions from hydroelectric reservoirs. *Ambio* 23: 164–165.
- Rosa L. P., Santos, M.A., Matvienko, B., Sikar, E., Lourenço, R.S.M. and Menezes, C.F. 2003. Biogenic gas production from major Amazon reservoirs, Brazil. *Hydrol. Process.* 17: 1443–1450.
- Rudd, J.W.M., Harris, R., Kelly, C.A. and Hecky, R.E. 1993. Are hydroelectric reservoirs significant sources of greenhouse gases? *Ambio* 22: 246–248.
- Santos, M.A., Rosa, L.P., Matvienko, B., Sikar, E. and Santos, E. D. 2006. Gross greenhouse gas emissions from hydro-power reservoir compared to thermo-power plants. *Energy Policy* 34: 481–488.
- Schlesinger W.H. 1997. *Biogeochemistry: An Analysis of Global Change*. 2nd ed. Academic Press, San Diego, California.
- Scranton, M.I., Crill, P., DeAngelis, M.A., Donaghay, P.L. and Sieburth, J.M. 1993. The importance of episodic events in controlling the flux of methane from an anoxic basin. *Global Biogeochem. Cycles* 7: 491–507.
- Sikar, E., Santos, M.A., Matvienko, B., Silva, M.B., Rocha, C.H., Santos, E., Bentes Junior, A.P. and Rosa, L. P. 2005. Greenhouse gases and initial findings on the carbon circulation in two reservoirs and their watersheds. *Verh. Internat. Verein. Limnol.* 29: 573–576.
- Sikar, E., Matvienko, B., Santos, M.A., Rosa, L.P., Silva, M.B., Santos, E.O., Rocha, C.H.E.D. and Bentes Jr, A.P. 2009. Tropical reservoirs are bigger carbon sinks than soils. *Verh. Internat. Verein. Limnol.* 30: 838–840.
- Sitaula B.K., Bakken L.R. 1993. N₂O Release from Spruce Forest Soil, Relation with Nitrification, CH₄ Uptake, Temperature, Moisture and Fertilisation. *Soil Biol Biochem* 25:1415–1421.
- Soumis, N., Lucotte, M., Larose, C., Veillette, F., and Canuel, R. 2007. Photomineralization in a boreal hydroelectric reservoir: a comparison with natural

- aquatic ecosystems, *Biogeochemistry*, 86, 123–135, 10.1007/s10533-007-9141-z.
- Soumis, N., E. Duchemin, R. Canuel and M. Lucotte 2004. Greenhouse gas emissions from reservoirs of the western United States. *Global Biogeochem. Cycles* 18: doi: 10. 1029/2003GB002 197.
- Stange F., Butterbach-Pahl K., Papen H., Zechmeister-Boltenstern S., Li C., Aber J. 2000. A Process-Oriented Model of N₂O and NO Emissions from Forest Soils. 2nd Sensitivity Analysis and Validation. *J Geophys Res* 105(D4): 4385–4398.
- Straskraba, M. and Tundisi, J.G 1999. Reservoir Water Quality Management. In: UNEP/ILEC Guidelines of lake management. V.9. Japan: ILEC (International Lake Environment Committee).
- Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y. 2002. Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects, *Deep-Sea Res.*, Part II, 49(9–10): 1601–1622.
- Therrien, J., Tremblay, A. and Jacques, A. 2005. CO₂ emissions from semi-arid reservoirs and natural aquatic ecosystems. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p. 233–250.
- Tremblay, A. and Bastien, J. 2009. Greenhouse Gases Fluxes from a New Reservoir and Natural Water Bodies in Québec, Canada. *Verh. Internat. Verein. Limnol.* Vol. 30, Part 6, p. 866–869.
- Tremblay, Varfalvy, L., Roehm, C. and Garneau, M. (eds.) 2005. *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, 732 pages.
- UNESCO/IHA 2008. Assessment of the GHG status of freshwater reservoirs: scoping paper. Working Group on Greenhouse Gas Status of Freshwater Reservoirs. International Hydrological Programme. 28p. IHP/GHG-WG/3.
- UNFCCC: Global Warming Potentials: http://unfccc.int/ghg_data/items/3825.php
- USEPA U.S. Environmental Protection Agency) 1997. Volunteer stream monitoring: a methods manual. Office of Water (4503F) – EPA 841-B97-003. United States.
- USEPA (U.S. Environmental Protection Agency) 2001. Managing lakes and reservoirs. 3 ed. Office of Water – EPA 841-B01-006. Washington, United States.
- USEPA (U.S. Environmental Protection Agency) 2009. Nitrous Oxide. Sources and Emissions. Retrieved 28 September 2009 from www.epa.gov/nitrousoxide/sources.html
- Valfarvy, L. 2005. potential contribution of hydro reservoirs to global warming: what is the real issue? Pages 7–23. In Santos, M.A. and Rosa, L.P. (eds.) *Global warming and hydroelectric reservoirs. COPPE/UFRJ, Eletrobrás, Rio de Janeiro*, 197 pages.
- Walter, B.P. and Heimann, M. 2000. A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate. *Global Biogeochem. Cycles* 14: 745–65.
- Wanninkhof, R. 1992. Relationship between gas exchange and wind speed over the ocean. *Journal of Geophysical Research*, 97: 7373–7382.
- Weiss, R.F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203–215.
- Weiss RF. 1976. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203–15.
- Yamamoto S, Alcauskas, J.B. and Crozier, T.E. 1976. Solubility of methane in distilled water and seawater. *J. Chem. Eng. Data.* 21: 78–80.

3. Field Manual

3.1 Introduction

3.2 Sampling considerations

3.3 Terrestrial system methodologies

3.4 Aquatic system methodologies

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3.1. Introduction

3.1.1. Objectives

Today there is worldwide debate about the role of freshwater reservoirs and their contribution to atmospheric GHG emissions. Most studies of reservoirs indicate that GHG emissions can significantly vary (up to two orders of magnitude) from one reservoir to another, or in the same reservoir for samples collected at different times of the year, or at the same times of year but in different areas (time/space variability). Studies so far have been conducted primarily in Canada (Tremblay et al., 2005), Finland (Huttunen et al., 2002), Brazil (Santos et al., 2005), French Guiana (Galy-Lacaux et al., 1997) and Laos.

This *Field Manual's* main goal is to provide objective and clear instructions on field methods and the equipment needed to estimate GHG emissions, giving qualified technicians and scientists a reliable reference for field GHG emission measurements in freshwater reservoirs. More specifically, the *Field Manual* includes instructions on how to conduct GHG measurements in terrestrial and aquatic ecosystems in terms of GHG emissions and carbon and nitrogen stocks.

The manual does not apply to routine reservoir monitoring in all existing and future reservoirs, but aims to establish a standard method that will make it easy to compare and transfer field data from surveyed reservoirs.

As such, it is meant to be a living and dynamic document, often updated.

3.1.2. Use of this *Field Manual*

The present version was developed to provide the standards for field measurements in a representative set of reservoirs. As part of the UNESCO/IHA GHG Project, the present version of the *Field Manual* is meant for use by qualified technicians and scientists to assess GHG emissions in a sample of representative sites worldwide.

As with the other sections of these *Guidelines*, this *Field Manual* has been developed to establish a standard methodology, and, as such, is not intended for general routine application to all reservoirs. Future versions can introduce a tiered approach as previously stated (see section 1.1.2), enabling other uses. The *Field Manual* is to apply world-wide for all types of climate and different

reservoir conditions, and for natural lakes or man-made reservoirs of all types and purposes. With the *Calculation Manual*, it sets the standards for estimating the net GHG emissions that arise from creating a reservoir in a river basin.

Figure 1.1 (section 1) demonstrates the use of this *Field Manual*, within the context of the *Guidelines*. At the end of this section, Appendix 3.1 provides internet links to reference documents and procedures, and Appendix 3.2 outlines equipment cost estimates.

3.2. Sampling considerations

To capture the net GHG emissions from a reservoir in a river basin, it is important to analyse the potential spatial and temporal variability in possible GHG emissions when designing the measurement campaign. The analysis should take into account how seasonal changes in climatic conditions, reservoir operations and carbon load may influence the temporal variability. When designing the spatial sampling, vegetation; land use (pre- and post-impoundment) and other anthropogenic activities; and hydrological, meteorological and limnological issues should be considered. Practical issues like accessibility, safety and other indirect implications should also be considered.

According to the UNESCO/IHA (2008), reservoirs should be compartmentalized (monitored section by section) to reflect regions with distinct behaviour in the reservoir and the predominant processes quantified in each of these regions. Different types of sampling stations may need to be chosen for long-term monitoring: stations at the upstream reach, and other points of inflow; stations along the longitudinal axis of the reservoir; stations in vegetated and non-vegetated littoral zones of the reservoir; stations in embayments (where they exist); stations close to the outlets, to understand the mixing of the water column upstream; and stations in the river downstream.

The number of sampling stations and the sampling frequency are defined according to the available budget, manpower and detailed objectives. They may be determined by adopting heuristic (or arbitrary) criteria or using statistical tools to ensure a desired accuracy.

The following sections present the main principles in planning field surveys, and describe how to determine the scope and objectives of sampling, as well as its spatial and temporal resolution.

Figures 3.1 and 3.2 present factors to be considered when developing a sampling plan, including station selection, spatial and temporal resolution, and monitoring. Figures 3.3, 3.4, 3.5 and 3.6 provide summaries of aquatic and terrestrial variables, associated measurement methods, and the advantages and constraints of those methods.

3.2.1. Steps and principles in planning field surveys

The following items should be considered when planning field surveys (*ASTM, 1997; UNFCCC, 2009*):

a. Scoping the project

- Describe the scope, approach to sampling and justification for it at an early stage.
- Specify objectives, boundaries (definition of the area affected by the reservoir – see Figure 3.7) and other scoping variables.
- Field campaigns should be planned by skilled professionals who know the field and understand the regional features affecting the project.

b. Literature/data review

- Collect existing pertinent data and information about the study site.
 - Consult the literature and historical records, and interview experts, government officials, and people familiar with the sites.
 - Consult topographic, geological, soil, vegetation and land-use maps, aerial photographs and satellite images.
 - Determine site history (changes in economic activities, including land use).
 - For terrestrial ecosystems, important variables include vegetation type, age of stand, soil type, regional climate, above- and below-ground biomass inventory, soil carbon content, soil physical and chemical properties, vegetation parameters, air temperature.
 - For aquatic ecosystems, important variables include sediment type, present water level, changes in water level, water flows, depth, reservoir operating procedures, and meteorological information.
- Inspect the site to check the accuracy of available information and to identify site characteristics needing more investigation.

c. Developing a sampling plan

- Sampling aims to obtain reliable, unbiased estimates of the mean or total value of key variables and their variability. Reliability can be expressed in terms of the probability that the sample value falls within a specified interval around the population value.
- The accuracy of a sample-based estimate increases directly with sample size. Before taking a sample, decide on the sample size required to achieve a given accuracy (see section 3.2.2). Note that sample design should take into account size and space-time heterogeneity.
- The choice of sample type depends on several factors, including the types of information to be collected through sampling; known characteristics of the population; and the cost of information gathering.
 - The sampling approaches include simple random, systematic, stratified random, cluster and multi-stage sampling (see section 3.2.2.1).
 - As the area covered by the reservoir and its watershed can be very large and influenced by land use, climate, geology, soil and reservoir characteristics, stratified sampling should be preferred over other sampling approaches whenever possible, i.e., whenever grouping variables are available. This approach consists of grouping cases into fairly homogeneous subpopulations and sampling each population independently. Stratification can increase efficiency through improving precision for a given sample size, and can ensure that estimates are made with equal accuracy in the various strata.
- Develop one or more conceptual models of the site based on existing information.
 - Prepare maps of the study site.
- Develop a detailed site investigation and sampling plan.
 - Review available regional and local information.
 - Interpret aerial photographs and other remote sensing data.
 - Select appropriate methods for collecting location data (latitude, longitude and altitude).
- Every project is site specific so it should have its own spatial and temporal planning for measurements.

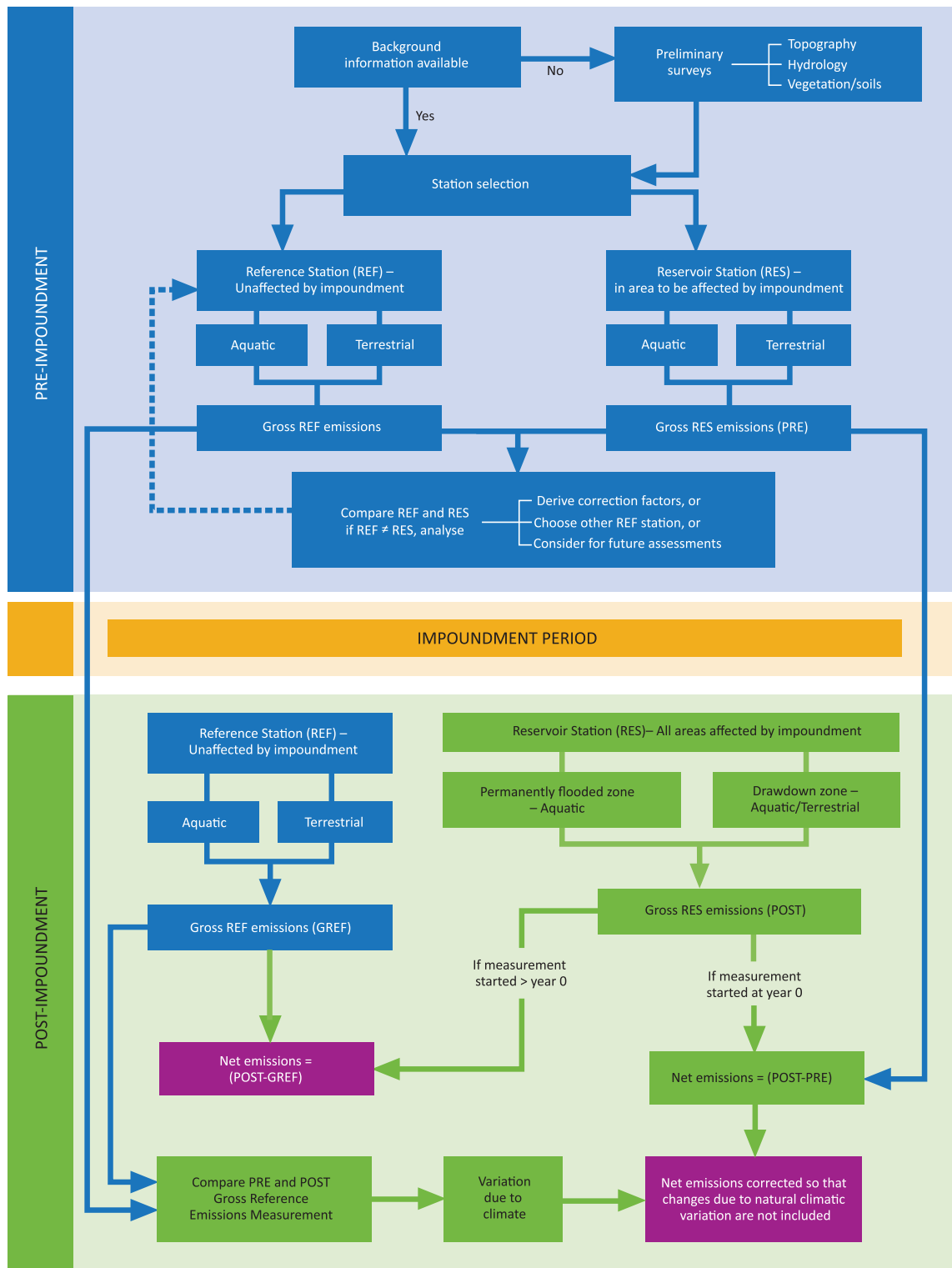


Figure 3.1: Scope of GHG monitoring programme for reservoirs

- Spatial and temporal resolutions are linked, and a balanced approach is needed in considering both. For example, if greater spatial than temporal variation is expected in a specific instance, more stations may be visited less often. If the opposite is true, a few representative stations may be visited more often or measurements may be taken continuously. The budget and resources available may influence planning.
- Measurements in space and time must be compartmentalized to get representative measurements and to take into account any zones with high emissions but a small surface area (or few occurrences over time).

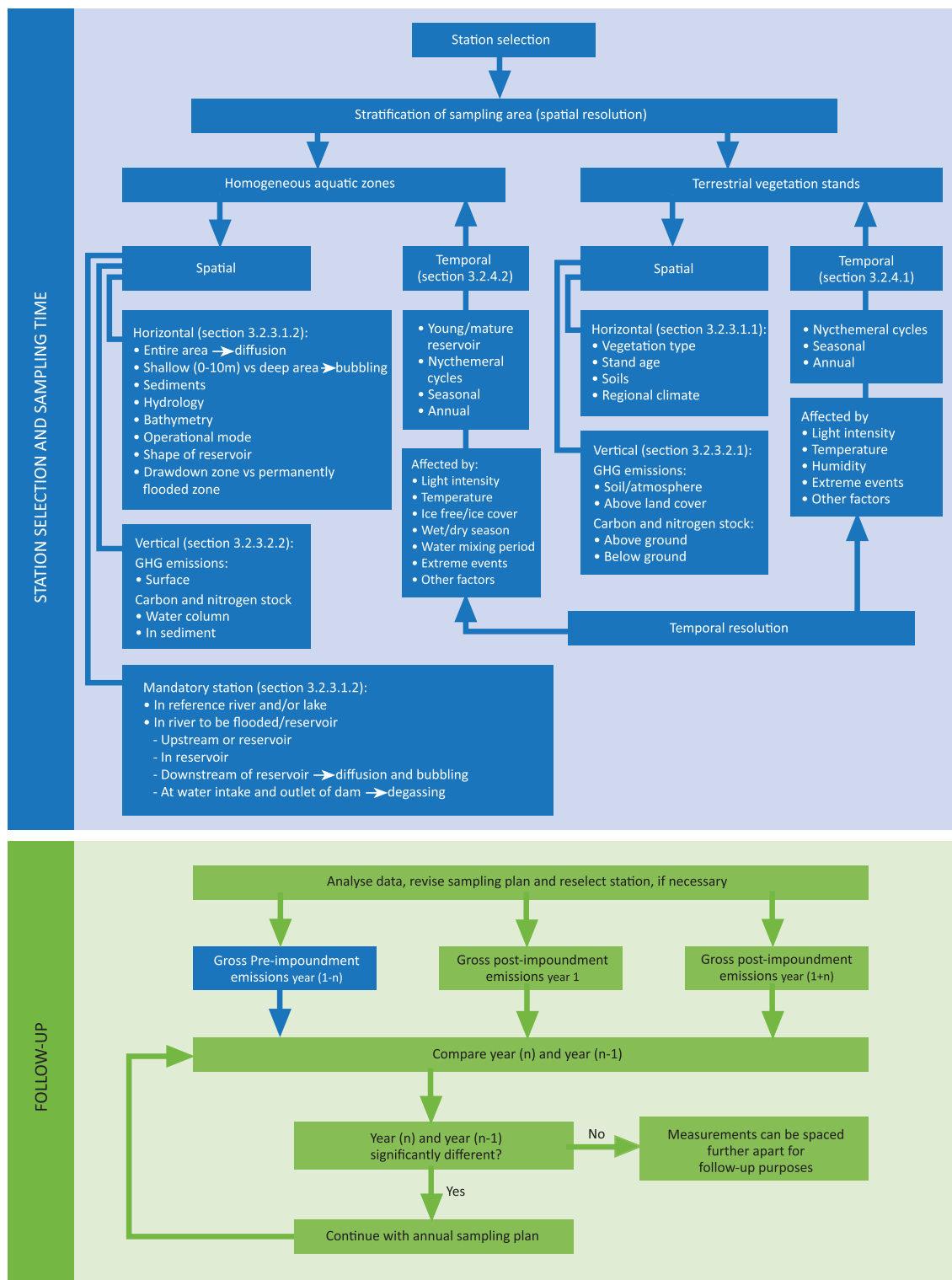


Figure 3.2: Spatial and temporal resolution of sampling plan

- As a general principle, flow-proportional sampling should be applied, i.e. more measurements should be performed in compartments (or at times) of higher expected flux. For example, an area (or period of day) with 50% of the expected flux should be covered by 50% of the measurements.
- The same principles should apply for pre- and post-impoundment measurements, for different systems (aquatic, terrestrial, downstream, upstream, etc.) and for different variables (GHG concentrations and fluxes, physical, chemical and biological variables, etc.).

- The spatial and temporal resolution must be subject to a multi-criteria approach, including confidence analysis of results and cost-benefit analysis, and may be modified for budgetary reasons.
 - Reference sites must be identified in both the aquatic and terrestrial ecosystems to ensure that normal variations due to climate or changes in land use are taken into account and not seen as reservoir effects. Reference sites may also be used to estimate net emissions when measurements begin after reservoir impoundment.
 - Replicate measurements must be used in the field to account for the variation within the method (for example, three diffusive fluxes may be measured with the chamber method). Replicate analysis can also be performed to account for the variation within the analysis method (for example, three subsamples may be analysed by gas chromatography).
- d. Field surveys**
- Perform field reconnaissance and on-site investigation.
 - Obtain representative samples and measurements for variables identified and selected.
 - Collect field samples and take measurements.
- e. Data analysis and sampling plan optimisation**
- Analyse field and laboratory data.
 - Assess spatial resolution of selected variables:
 - Horizontal (surface): upstream of the river/reservoir (in both the river and catchment), in the river/reservoir (in the river channel and drawdown zone), and downstream of the river/reservoir (in both aquatic and terrestrial systems).
 - Vertical (depth).
 - Assess the temporal resolution of selected variables that may affect GHG emissions:
 - Diurnal – light intensity, primary production, respiration rate, surface heat loss and reservoir operating mode (water level).
 - Seasonal – wet and dry season, ice cover, snowmelt, seasonal mixing of water and reservoir operating mode (water level).
 - Annual – climatic conditions (precipitation, run-off, temperature, etc.) and reservoir operating mode (water level).
 - Refine the sampling plan based on the analysis of results. This is an iterative process whose length depends on the complexity of the study site and budgetary constraints. The results and analysis from an initial comprehensive survey will help determine representative spots, so continuous or seasonal measurements may be taken at fewer representative sampling stations established in these areas.
 - Spatial and temporal resolution must be an integral part of planning and evaluation, using an adaptive measurement design (i.e. revising the resolution after analysing the initial data).

3.2.2. Determination of the sampling effort

Depending on the age of the reservoir, the complexity of the site, the objective of the survey², and the resources available, a different number of gauging stations can be adopted for each site. This number may be arbitrarily determined, based on the characteristics of the study, or statistical tools can be used to help design the sampling effort, to guarantee a specific level of accuracy. It can vary from a few stations³ (at least able to characterise the main inflow into the reservoir, the GHG emissions in the reservoir main body, and the conditions downstream of the reservoir outlet) up to many stations (with a detailed description of the GHG emissions on the affected area).

This section introduces a set of methods to determine the number and location of gauging stations, and the frequency and duration of the measurements.

It is important to emphasise that this methodology has to assess the information regarding pre- and post-impoundment conditions:

- In the case of pre-impoundment conditions, it has to take into consideration the catchment/

² The required level of accuracy will differ according to the study's objective. Different purposes (such as applying for support under the CDM, performing national GHG inventories, complying with national environmental requirements, or performing scientific research studies) would imply different requirements. For example, the CDM-EB47 (2009) states that 'where there is no specific guidance in the approved methodology, project proponents shall choose 90/10 precision as the minimum precision targets for the most important data collection efforts on the most important data variable affecting the emission reductions of the project activity'. This means a sample-based estimate should have a 90% probability of falling in a range of $\pm 10\%$ of the true population value. Other requirements could be necessary for other applications.

³ The use of only a few stations may lead to significant uncertainties with regard to the data obtained.

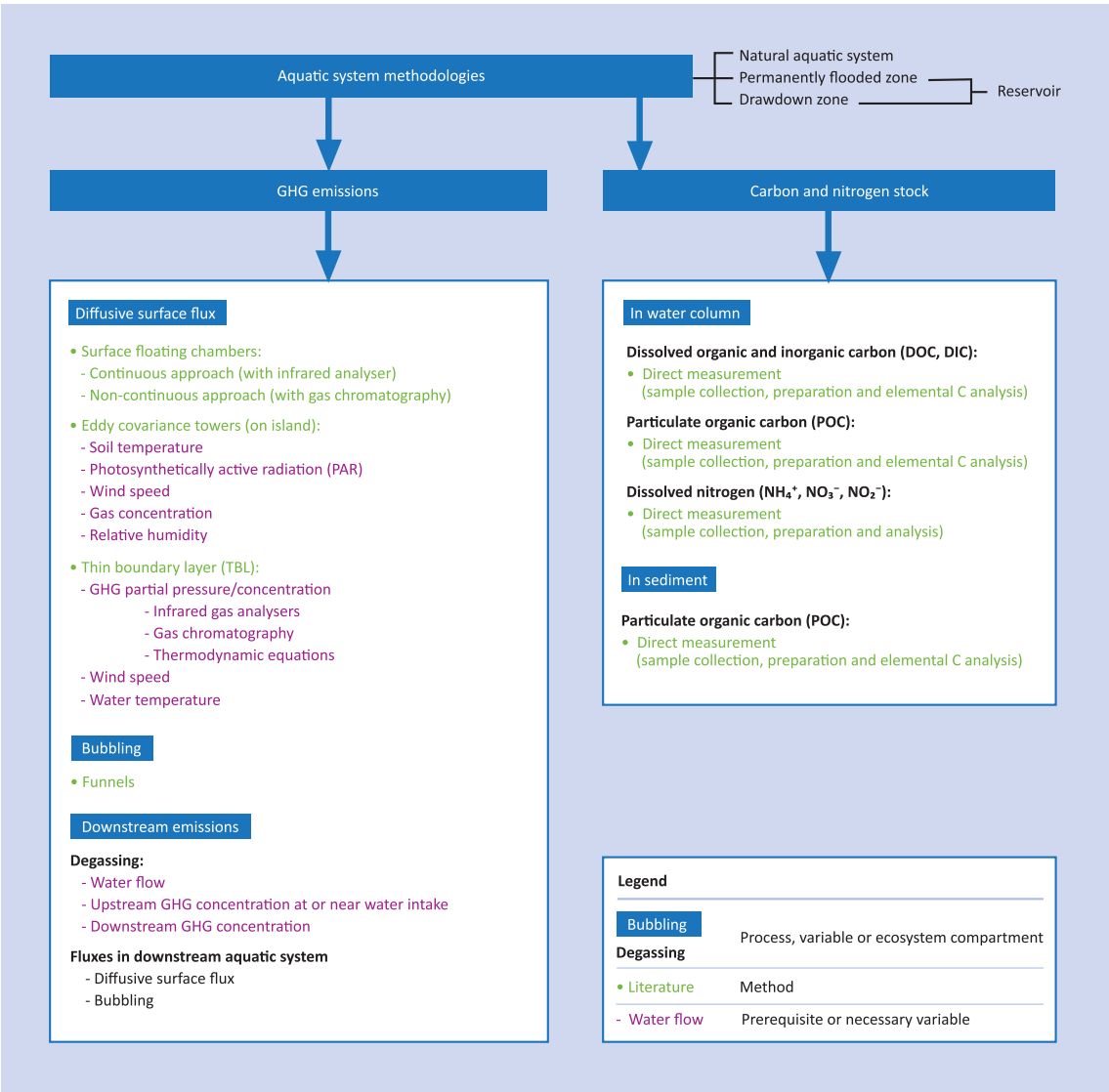


Figure 3.3: Aquatic systems methodologies

reservoir terrestrial and aquatic environments and the area downstream of the reservoir site, and must also assess carbon stock. If the impoundment is already in place, literature or measurements (or both) at reference sites may be useful. When using reference sites, measurements should be taken in the catchment at representative sites for all relevant land and water use in a sufficiently precise time series to cover seasonal changes.

- In the case of post-impoundment conditions, emissions from the catchment, in the reservoir, and downstream of the reservoir site have to be estimated.

3.2.2.1. Sampling approaches and applicability

Several different sampling approaches are available, to be adopted according to several criteria, including the survey's objective, the characteristics of the data to be collected, the desired accuracy of the estimates, and the available budget and resources. Some of the most common sampling methods (simple random sampling, systematic sampling, stratified random sampling, cluster sampling) are summarized in this section, with guidelines on where best to use each of them. Complete descriptions of these methods can be found in Hansen (1953), Cochran (1977), Groves (1989, 2004), Kish (1995), Levy and Lemeshow (1999), and UNFCCC (2009). UNFCCC (2007) also provides guidance on sampling approaches for reservoirs.

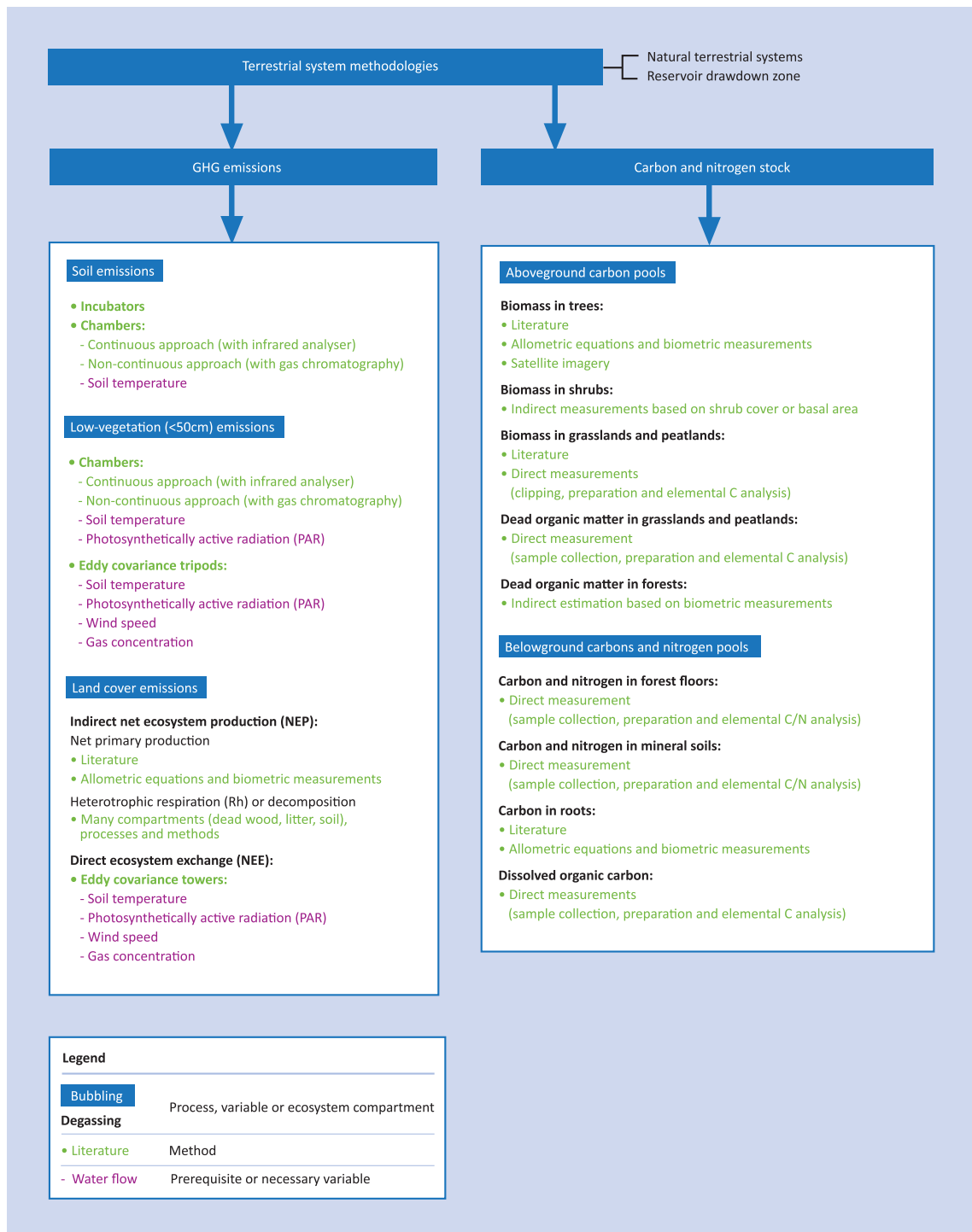


Figure 3.4: Terrestrial systems methodologies

In all the approaches, take care to ensure that the samples are drawn in a manner that avoids any systematic bias and that the data collection minimizes non-sampling errors. To achieve these goals, practitioners are expected to follow sound practices in designing samples and administering surveys and field measurements. It is also important to stress that, in many cases, the location of the equipment can depend on site or working conditions, giving little opportunity for random and

systematic sampling. In most cases, the reservoirs should be stratified or cluster sampled.

3.2.2.1.1. Simple random sampling

A simple random sample is a subset of individuals (a sample) chosen from a larger set (a population). Each individual is chosen randomly and entirely by chance, such that each individual has the same probability of being chosen at any stage during the sampling process, and each subset of k individuals

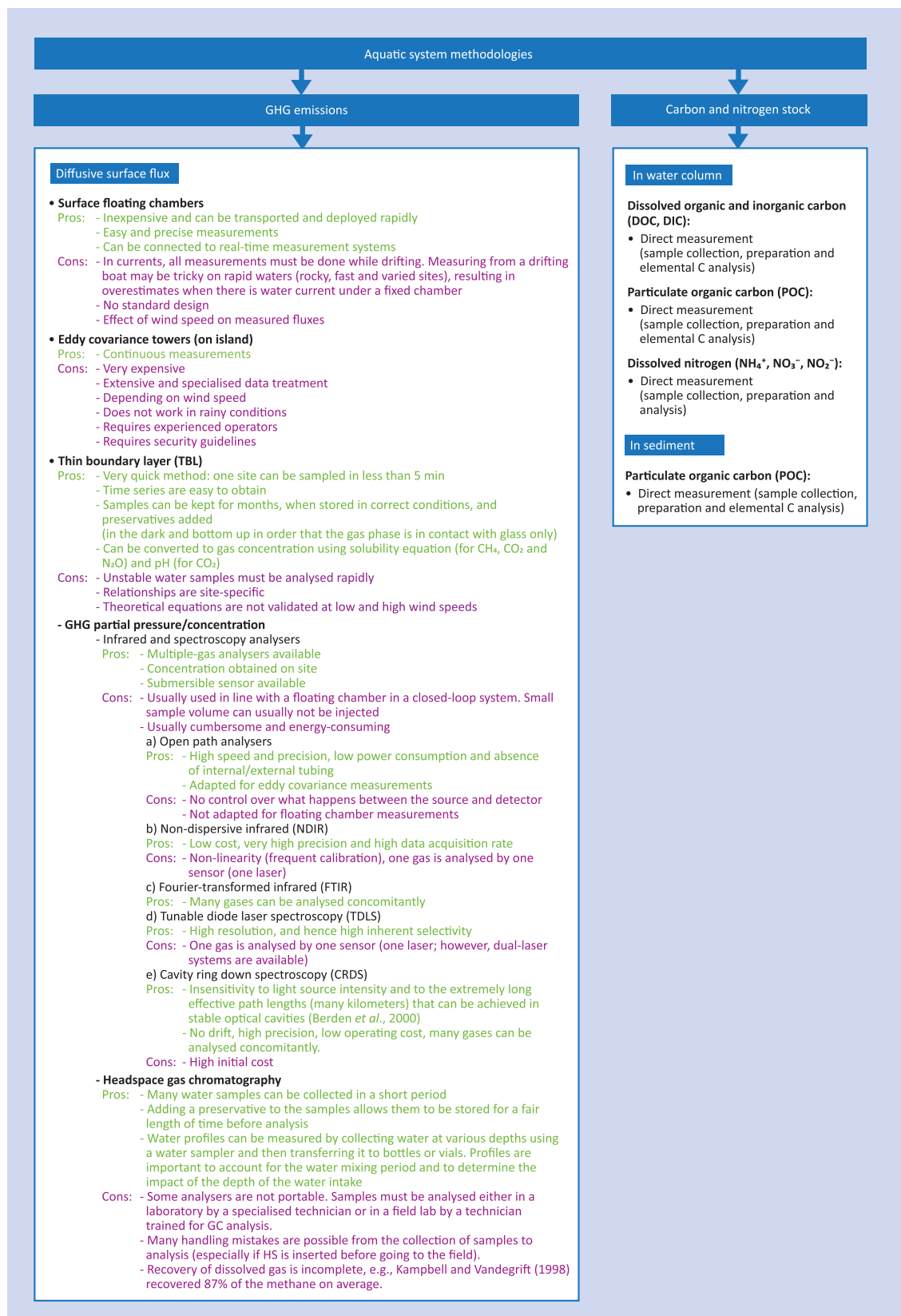


Figure 3.5: Aquatic systems methodologies – pros and cons

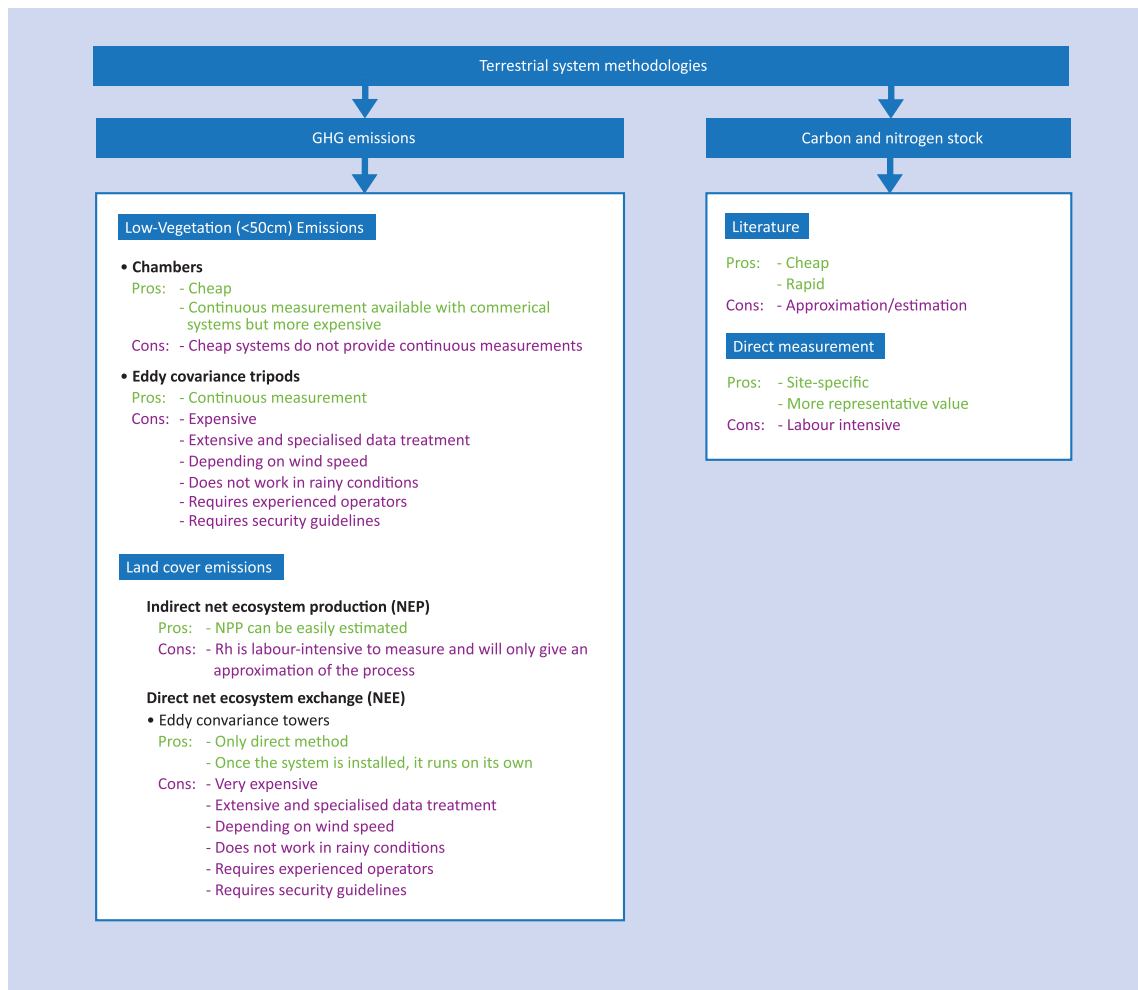


Figure 3.6: Terrestrial systems methodologies – pros and cons

has the same probability of being chosen for the sample as any other subset of k individuals (Yates *et al.*, 2008). Simple random sampling is the most straightforward method for designing a sample.

Under simple random sampling, each case in the sample frame (an exhaustive list of all the cases in the population) has an equal probability of being selected into the sample. The mean value of the measurement from a random sample is an unbiased estimate of the true population mean; hence repeated independent samples will provide estimates that are, on average, equal to the population mean.

Random sampling methods are recommended when more efficient sampling techniques are unfeasible or impractical, or where the population is relatively homogeneous with respect to the object of the study. For example, other sampling methods typically require more information from the sample frame, such as a stratification variable.

Simple random sampling is free of classification error, and it requires minimum advance knowledge

of the population. Its simplicity also makes it relatively easy to interpret data collected. For these reasons, simple random sampling best suits situations where limited information is available about the population, and data collection can be efficiently conducted on randomly distributed items, or where the cost of sampling is small enough to make efficiency less important than simplicity. If these conditions do not apply, stratified sampling or cluster sampling may be a better choice.

3.2.2.1.2. Systematic sampling

Systematic sampling is a statistical method involving the selection of elements from an ordered sampling frame. The most common form of systematic sampling is an equal-probability method, in which every k th element in the frame is selected, where k , the sampling interval (sometimes known as the 'skip'), is calculated as:

$$k = \text{population size (N)} / \text{sample size (n)}.$$

Using this procedure, each element in the population has a known and equal probability

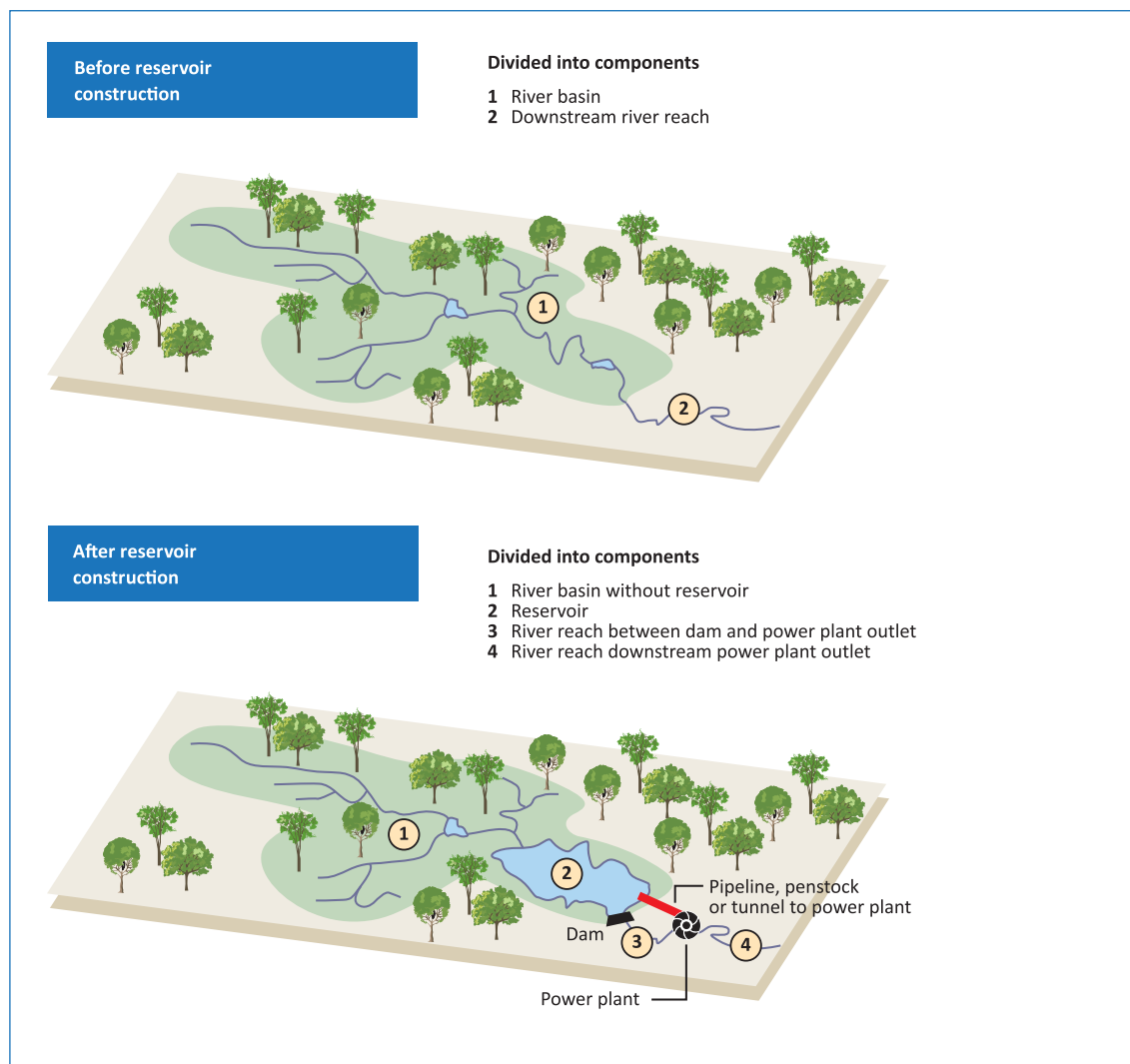


Figure 3.7: Boundaries for reservoir projects

Source: UNESCO/IHA, 2008

of selection. This makes systematic sampling functionally similar to simple random sampling. It is however, much more efficient (if variance within systematic sample is more than variance of population).

Systematic sampling is to be applied only if the given population is logically homogeneous, because systematic sample units are uniformly distributed over the population. Any pattern would threaten randomness.

Systematic sampling is a relatively simple method to apply, which makes it easily understood and useful when field workers are asked to sample a subset of units based on their inspections. It is also useful when the population is organized in some temporal or other natural order without a trend or cyclical pattern.

3.2.2.1.3. Stratified random sampling

Another method is stratified random sampling. When sub-populations vary considerably, it is advantageous to sample each subpopulation (stratum) independently. Under stratified random sampling, the population is divided into relatively homogeneous subgroups, called strata. The strata should be mutually exclusive: every element in the population must be assigned to only one stratum. The strata should also be collectively exhaustive: no population element can be excluded.

Stratification can increase the efficiency, i.e., produce a gain in precision for a given sample size, if the cases within each stratum are more homogeneous than across strata.

If population density varies greatly within a region, stratified sampling can also ensure that estimates will be equally accurate in different parts of the

region, and that comparisons of sub-regions can be made with equal statistical power.

Stratified random sampling is most applicable to situations where there are natural groupings of subjects whose characteristics are more similar within a group than across groups. It requires that the grouping variable be known for all subjects in the sample frame. Stratification can increase the efficiency, i.e., improve precision for a given sample size, if the cases within each stratum are more homogeneous than across strata.

3.2.2.1.4. Cluster sampling

Clustered sampling refers to a technique where the population is divided into sub-groups (clusters), and the sub-groups are sampled, rather than the individual elements to be studied. Cluster sampling is used when 'natural' groupings are evident in a population. In this technique, the total population is divided into sub-groups (clusters), and a sample of the groups is selected.

In contrast to stratified sampling, where the variable of interest is grouped into a relatively small number of homogeneous segments, there are many clusters of variables, and there is no expectation that the variables in each cluster are more homogeneous than the overall population.

One version of cluster sampling is area sampling or geographical cluster sampling. Clusters are defined by geographical areas. Because a geographically dispersed population can be expensive to survey, greater economy than in simple random sampling can be achieved by treating several respondents in a local area as a cluster. Usually the total sample size needs to be increased to achieve equivalent precision in the estimates, but cost savings may make that unfeasible.

There are at least two reasons for using a clustered sampling approach to collect data. The first is cost. If a significant component of the cost of data collection is travel time between sites, then it may make sense to monitor all of the equipment at individual locations to reduce that cost component. Under that approach, it will typically be necessary to meter more samples than under random sampling to achieve a given level of precision. But the cost saving may more than offset any negative effects on sample precision, allowing for a larger sample for any given budget, with greater precision.

The second reason is the ease of constructing the sample frame. In some cases where the programme participant is collecting baseline

information, it may be impossible to enumerate the population of different species from which to draw the sample. But it is possible to enumerate the clusters. In that situation, the programme participant could sample the clusters and conduct an inventory of the species in the chosen units.

3.2.2.2. Sample precision requirements: desired precision/expected variance and sample size

Reservoirs vary enormously in size, from tiny to over 2,000 km² in surface area. Quantifying processes at the entire scale of these ecosystems can be a significant challenge, particularly if these processes are known to vary considerably in both space and time. GHG emissions from natural and man-made ecosystems are the result of the net balance between the production and assimilation/consumption of the reactive gases through a variety of mostly biological and photochemical processes (Prairie, 2009). When terrestrial systems are included, the complexity of the situation increases considerably.

Devising a single sampling protocol capable of characterizing the GHG emissions with a desired precision is at best difficult and depends largely on the spatial heterogeneity of the factors influencing emissions at a local scale and on the superimposed physical homogenization mechanisms acting on these processes. While relatively little is known about the factors driving the spatial and temporal variability of GHG emissions in reservoirs, there is a sufficiently large empirical base to use as guidance to objectively define sampling protocols (Prairie, 2009).

The number of effective and independent samples needed to estimate a statistical mean depends on 1) the variability of the phenomenon to be sampled and 2) the level of precision desired. More samples will be needed for a highly variable phenomenon (in both space and time).

The number of stations may be determined arbitrarily or statistically to achieve a specific level of accuracy.

If a reservoir being investigated has already been subject to GHG measurements, available data should be used to determine the variability and mean fluxes. This estimation should be followed with a statistical method to calculate the number of samples needed to achieve the acceptable confidence levels and to meet the GHG sampling programme's objectives (Prairie, 2009).

Table 3.1: Mean-variance relationships and average sample size (Prairie, 2009)

Variable analysed	Mean-variance relationship	Coefficient of determination (r^2)	average sample size expression
$p\text{CO}_2$ (μatm)	$S^2_{p\text{CO}_2} = 1.05 \times 10^{-5} \overline{p\text{CO}_2}^{3.14}$	$r^2 = 57\%$	$n = \frac{1.05 \times 10^{-5} \overline{p\text{CO}_2}^{1.14}}{PL^2}$
$p\text{CH}_4$	$S^2_{p\text{CH}_4} = 3.70 \overline{p\text{CH}_4}^{1.76}$	$r^2 = 85\%$	$n = \frac{1.11}{PL^2}$
CO_2 flux	$S^2_{\text{CO}_2 \text{ flux}} = 0.21 \cdot \overline{\text{CO}_2 \text{ flux}}^{2.05}$	$r^2 = 55\%$	$n = \frac{0.21}{PL^2}$
CH_4 flux	$S^2_{\text{CH}_4 \text{ flux}} = 0.88 \cdot \overline{\text{CH}_4 \text{ flux}}^{1.95}$	$r^2 = 74\%$	$n = \frac{0.82}{PL^2}$

Where: S^2 = variance; \bar{x} = average of x ; n = sample size;
 r^2 = coefficient of determination (% of the variation explained by the expression);
 PL = Precision Level desired (as a coefficient of variation of the mean)

Table 3.2: Sampling size required for different levels of precision in the mean (Prairie, 2009)

Variable analysed	Range	Precision level desired			
		20%	15%	10%	5%
$p\text{CO}_2$ (μatm)	200-1000	1	2	3	11
	1000-2500	2	3	8	31
	2000-5000	4	8	17	69
$p\text{CH}_4$	All values	28	49	111	444
CO_2 flux	All values	5	9	21	84
CH_4 flux	All values	21	36	82	328

According to Prairie (2009), when there is no information available, the number of sampling stations needed can usually only be estimated after statistical analysis of a preliminary sampling programme in the best of cases. Because the CDM programme requires monitoring of GHG emissions, it is unlikely that a preliminary survey can be done. The number of samples theoretically required is often unrealistic and technical, and economic constraints have to be considered in selecting the number of sampling stations in the study area. Therefore, alternative approaches are needed to establish the number of stations (spatial coverage) and the number of field campaigns (temporal coverage).

Two different studies using available data are described: one developed by Prairie (2009), using data from 121 reservoirs from boreal, tropical and temperate reservoirs; and the other, presented by

UNFCCC (2007), applying a bootstrap method to field data from a boreal reservoir that have been adjusted to known estimates of tropical reservoirs.

The study by Prairie (2009) used a data set provided by Hydro-Quebec, consisting of over 7,200 measurements of gas flux (CO_2 and/or CH_4) in a total of 121 reservoirs. A regression analysis was developed to estimate the average number of samples needed to get a desired precision level. Mean-variance relationships were fitted for four important components of greenhouse gas emissions from reservoirs: $p\text{CO}_2$, $p\text{CH}_4$, CO_2 flux and CH_4 flux. The expressions obtained are presented in table 3.1, with the correspondent coefficient of determination (r^2). Table 3.2 presents the number of samples needed to get a given level of precision in the mean and for different ranges of the analysed variables.

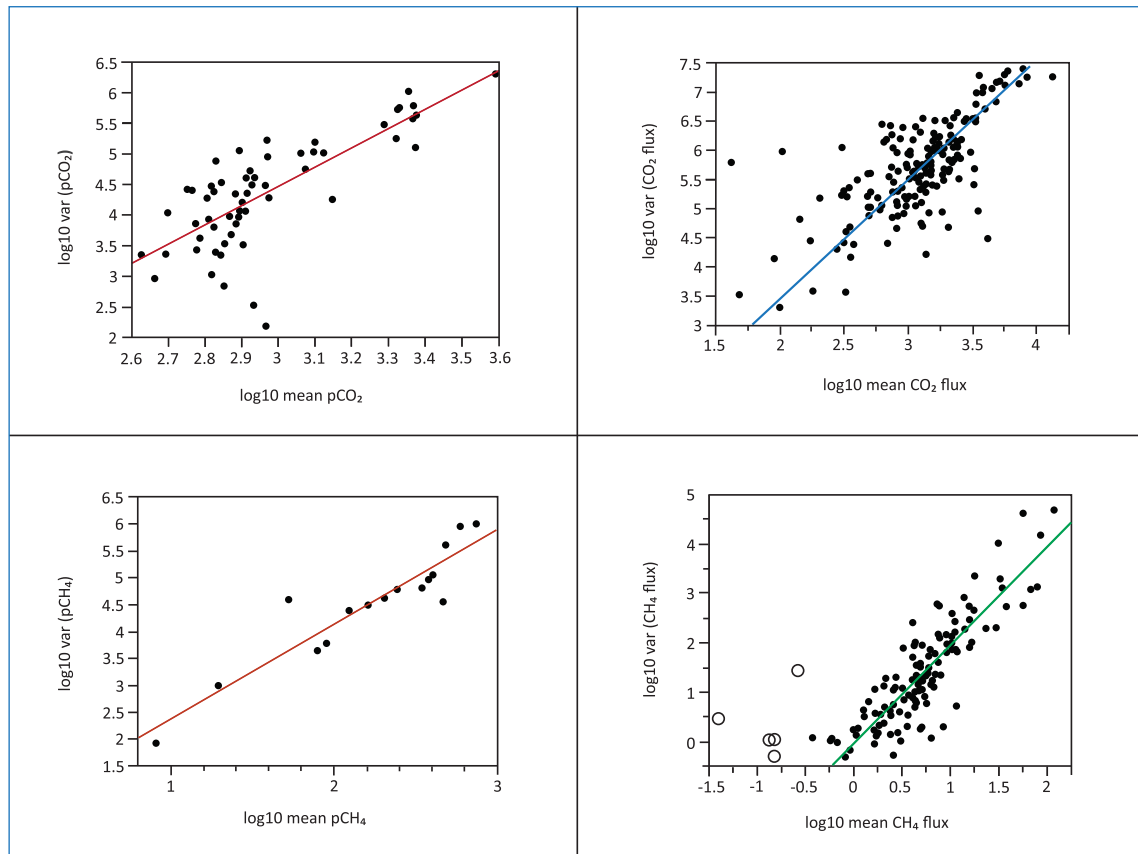


Figure 3.8: Mean-variance relationships as determined by Prairie

These results show that methane is much more spatio-temporally variable than carbon dioxide and that far more samples are needed to get the same level of precision in the estimated average.

Figure 3.8 shows the mean-variance relationships determined by Prairie (2009), where the fitted power function is represented by a straight line on a double logarithmic scale. The scatter presented in the graphs is proportional to the r^2 value of the fitted expressions (% of the variation explained by the expression), and indicates the uncertainties in the estimations.

Please note that the number of samples estimated according to Prairie (2009) represents the average number needed to get the precision level (and not the minimum number of samples). On average, the specified number of samples should suffice for any given field campaign. Some reservoirs will require fewer samples and others will require more samples to achieve the same precision, according to the reservoir's particular spatial/temporal variability. The adopted expression for the estimation of the average sample size necessary at a given precision has to be used with caution, as it may underestimate the true sampling effort needed for particularly variable reservoirs.

The study presented by UNFCCC (2007) applied a bootstrap method to determine the uncertainty of the estimate for different scenarios of sampling effort. This approach is based on real field data from a boreal reservoir that have been adjusted to known estimates of tropical reservoir, assuming that the reservoir being investigated will behave following the same distribution as the data used for the simulation. An uncertainty of less than 10% was arbitrarily defined to determine the level of effort required using different combinations of sampling stations and field campaigns. Confidence intervals of GHG emissions estimated by the bootstrap method are presented in Tables 3.3 and 3.4, for 30 and 20 stations respectively per sampling campaign. For a better visual representation, the total average fluxes from Tables 3.3 and 3.4 are presented in Figure 3.9.

The authors concluded that the different sampling strategies simulated indicate that a global error of $\pm 10\%$ can be reached. The global error between 30 and 20 stations is very similar, but 30 stations should be selected when greater variation is expected, to have a more representative sampling strategy. Finally, the simulations also reveal that four sampling campaigns are sufficient to attain

Table 3.3: Bootstrap analysis results: annual CO_{2eq} budget (Gg of CO_{2eq}) and its 95% confidence interval (CI) for 30 stations at each sampling campaign

		Number of sampling campaigns				
		2	3	4	5	6
CO₂ diffusion	Upper CI	53.6	51.7	50.7	50.0	49.7
	Average	44.2	44.3	44.5	44.4	44.4
	Lower CI	36.4	37.9	38.8	39.4	39.7
CH₄ diffusion	Upper CI	3.40	3.31	3.24	3.20	3.16
	Average	2.86	2.84	2.85	2.85	2.85
	Lower CI	2.37	2.44	2.48	2.53	2.56
N₂O diffusion	Upper CI	0.33	0.31	0.30	0.30	0.30
	Average	0.25	0.25	0.25	0.25	0.25
	Lower CI	0.19	0.20	0.21	0.21	0.22
CH₄ bubbling	Upper CI	0.61	0.58	0.56	0.57	0.56
	Average	0.48	0.48	0.48	0.48	0.48
	Lower CI	0.36	0.38	0.40	0.40	0.40
CH₄ degassing	Value	48	48	48	48	48
Total	Upper CI	105	103	102	102	101
	Average	96	96	96	96	96
	Lower CI	88	89	90	91	91

Table 3.4: Bootstrap analysis results: annual CO_{2eq} budget and its 95% confidence interval (CI) for 20 stations at each sampling campaign

		Number of sampling campaigns				
		2	3	4	5	6
CO₂ diffusion	Upper CI	53.1	51.6	50.4	49.6	49.2
	Average	43.9	43.9	44.0	43.9	43.8
	Lower CI	35.9	37.3	38.2	38.8	39.4
CH₄ diffusion	Upper CI	2.81	2.73	2.69	2.66	2.61
	Average	2.40	2.40	2.40	2.39	2.39
	Lower CI	1.99	2.07	2.13	2.15	2.17
N₂O diffusion	Upper CI	0.33	0.31	0.30	0.30	0.29
	Average	0.24	0.24	0.24	0.24	0.24
	Lower CI	0.16	0.18	0.18	0.19	0.19
CH₄ bubbling	Upper CI	0.59	0.57	0.58	0.56	0.55
	Average	0.47	0.47	0.48	0.47	0.47
	Lower CI	0.37	0.39	0.38	0.39	0.40
CH₄ degassing	Value	48	48	48	48	48
TOTAL	Upper CI	104	103	102	101	100
	Average	95	95	95	95	95
	Lower CI	87	88	89	90	90

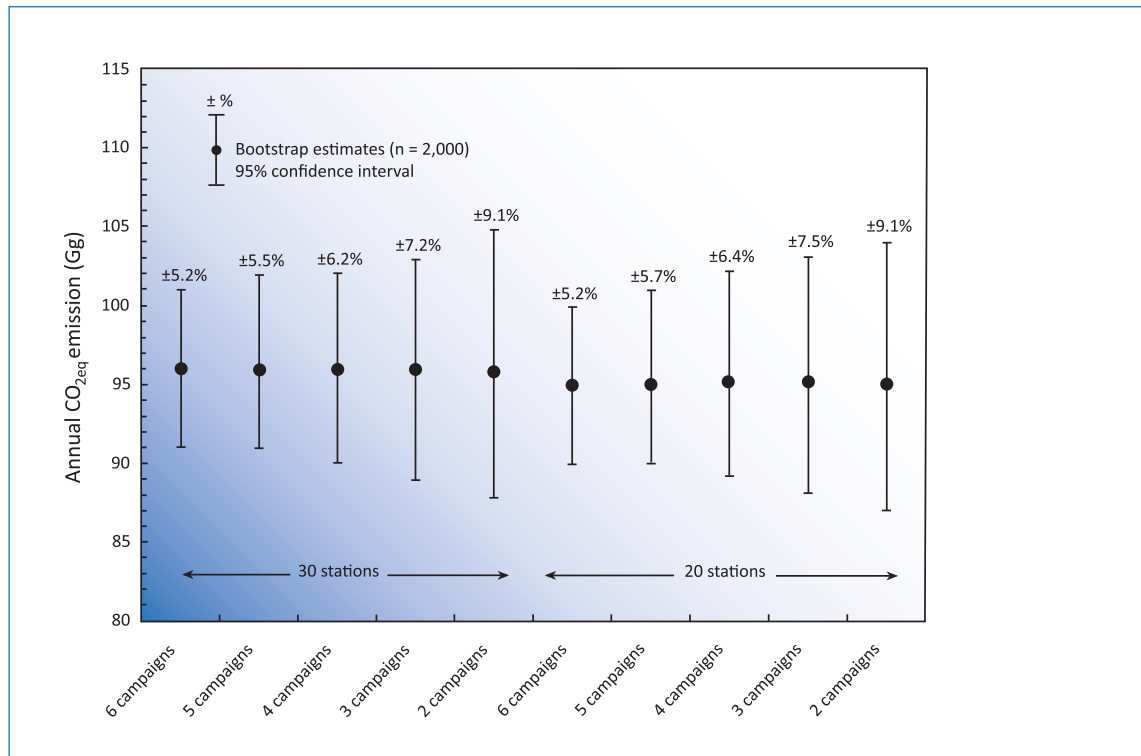


Figure 3.9: Summary of the bootstrap analysis for 2 to 6 campaigns and 20 and 30 stations

an acceptable global error of $\pm 6.2\%$. Increasing the number of campaigns will only provide a small gain in confidence interval. More than four sampling campaigns should be considered if seasonal variations are more important than the assumptions of this study.

Giving the similarity of results from 20 and 30 stations on the UNFCCC study, and adopting a level of precision of 10% in Prairie's study, both presented studies seem to suggest choosing 20 stations for CO₂ flux emissions. However, any of these approaches should be adopted with care, and specific case checking is always recommended. Many uncertainties are still present in the data. Little is known of the factors driving the variability in space and time of GHG properties (partial pressure and flux) at the ecosystem scale, so more field measurements are needed for a better understanding of the processes and better definition of the required sampling efforts.

3.2.3. Spatial resolution of sampling stations

The number of stations depends partly on the accuracy and confidence limits required. The number of stations may be determined arbitrarily or statistically to achieve a specific level of accuracy, as described in section 3.2.2.2. Non-parametric statistics are preferable for processes that may not have a normal distribution. Alternatively, the number

of stations may be determined using the cumulative average principle (i.e., by plotting the average of measurements vs. the number of measurements and seeing where the variability of the cumulative average levels out). The following sections present some basic criteria regarding horizontal and vertical spatial resolution for terrestrial and aquatic ecosystems, as well as on the drawdown zone.

3.2.3.1. Horizontal resolution

3.2.3.1.1. Terrestrial ecosystems

In terrestrial ecosystems, forest land may be stratified based on several factors to reduce the within-class variation in growth rate and other forest variables (IPCC, 2006). For instance, information on land use and land cover changes (LULCC), vegetation composition and biomass, age of forest stands, topography, soils, geology and climate may provide valuable insights regarding GHG emissions and carbon and nitrogen stock in terrestrial environments. Homogeneous forest stands, in representative vegetation classes, should be identified for the selection of sampling station.

3.2.3.1.2. Aquatic ecosystems

The shape of the reservoir (linear vs. dendritic), and the number and type of inflows to the river/reservoir, influence the heterogeneity of the river/reservoir and thus the number of stations required to effectively represent it (Figure 3.10).

Reference sites must also be chosen for control purposes when monitoring studies are planned and to determine net GHG emissions when no pre-impoundment data are available. It is recommended that a small number of lakes and rivers are chosen; these should be unaffected by anthropogenic water-level fluctuations and located near the reservoir.

It is mandatory to have at least one representative station upstream, one within and one downstream of the river/reservoir, so inflows and outflows to the river/reservoir can be monitored before and after impoundment.

Diffusion is expected to occur over the entire surface of the reservoir; whereas, in many cases, bubbling is more likely to occur in the area where the depth is between 0 and 10 m (although bubbling has on occasion been observed at depths of over 10 m). The horizontal resolution at a sampling station will thus vary, depending on the GHG emission pathway being measured or estimated. So, to get credible whole-system estimates, it is important to measure at different depths/distances to shore including at very shallow locations, to get credible whole system estimates.

3.2.3.1.3. Drawdown zone

All aquatic stations should be classified as being either in the drawdown zone or in the permanently flooded water body, because GHG emissions differ between these zones due to the presence/absence of vegetation and also because of drying of exposed sediments in the drawdown zone. Representative stations should be identified in each category. The period when the drawdown zone is flooded should be identified so that stations there can be identified as terrestrial or aquatic, and so that all seasons (with their varying water levels) are sampled equally. Diffusion and bubbling emissions can be expected to occur in the drawdown zone.

3.2.3.2. Vertical resolution

3.2.3.2.1. Terrestrial ecosystems

In terrestrial ecosystems, flux measurement systems determine the vertical resolution. Chambers can measure soil/low vegetation emissions, and soil emissions can be inferred from incubators, while eddy covariance (EC) systems measure fluxes through the atmosphere above the land cover. Ideally, measurement from both strata

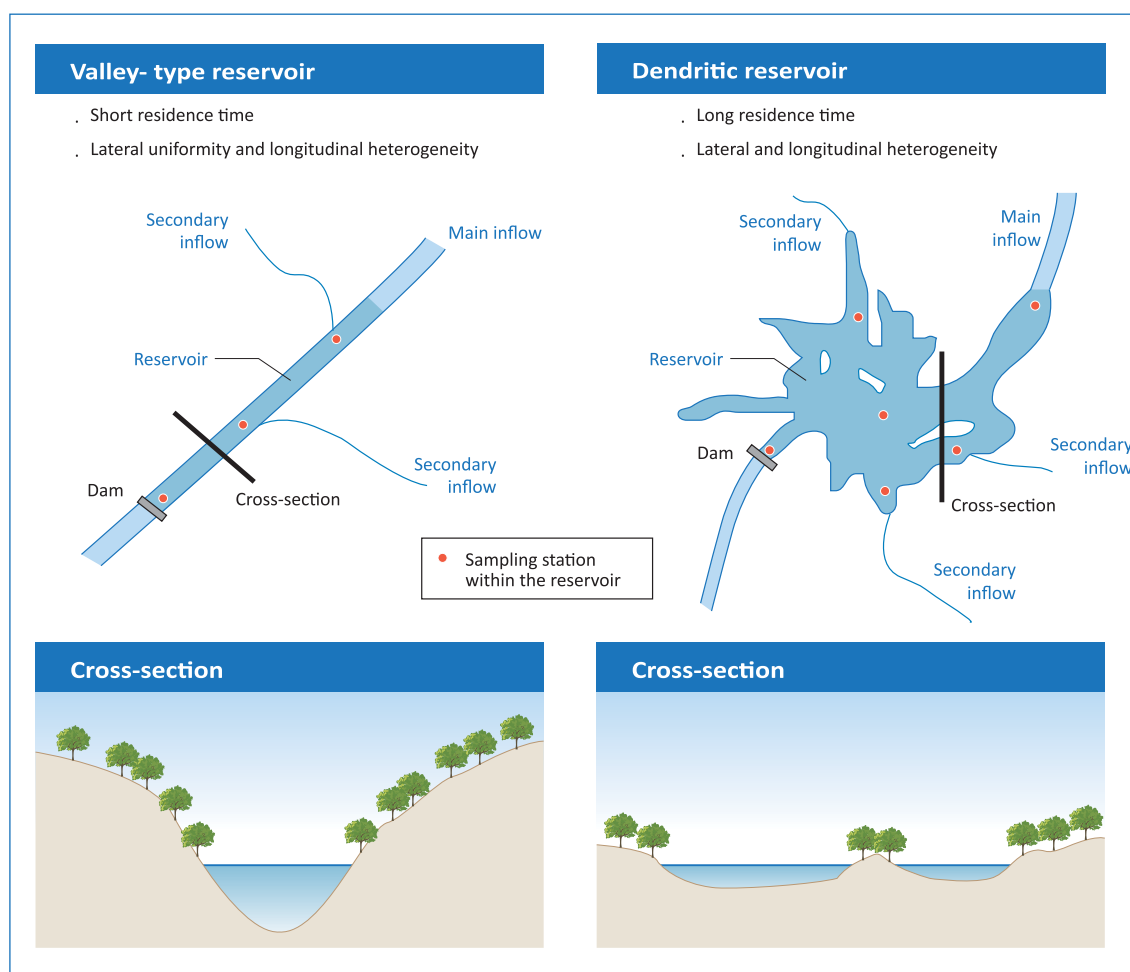


Figure 3.10: Reservoir types

(above the soil and above the land cover) should be taken, but this is usually not feasible.

Carbon and nitrogen stock values may be estimated or measured at various levels: aboveground biomass from trees, shrubs and low vegetation, as well as belowground biomass from soil and roots. Carbon in soil should be measured at incremental depths up to 50 cm (e.g., 0-10 cm, 20-30 cm and 40-50 cm).

3.2.3.2.2. Aquatic ecosystems

In aquatic ecosystems, diffusive water-air interface GHG flux measurements/estimates are conducted at the water surface only, using the floating chamber method or the thin boundary layer (TBL) method. Flux chamber measurements or measurements of flux into submerged inverted funnels can be used to capture ebullition.

It is important to measure GHG concentrations at various depths near the water intake for degassing estimates (reservoirs only) and at other representative stations in the river/reservoir to determine the impact of water mixing in regions where this phenomenon occurs. Alternatively, good data for estimating degassing can also be got by measuring GHG concentrations in the hydraulic circuit inside the power house (at the lowest level of the power house), before the water passes through the turbines.

Water samples for carbon and nitrogen stock measurements should be collected at several depths to represent the entire water column. The use of hydrodynamic models is a good tool to estimate water depths before taking the proper measurements. Estimating carbon and nitrogen stocks at measurement points inside the power house can be an alternative to getting water mixed from different depths.

Depth profiling of certain physicochemical variables should be performed at a minimum number of stations to determine whether stratification occurs.

3.2.4. Temporal resolution of sampling

Pre-impoundment inputs from the contributing areas should be determined before reservoir construction; but they may be measured after construction if the post-impoundment upstream catchment has not been changed from the pre-impoundment conditions or if reference sites near by can be used. This will affect net emission calculations (Figure 3.1: purple boxes).

Temporal resolution must be established based on several criteria or sampling constraints, as described below.

- **Practicability.** It is probably more practical to cover temporal variability by taking continuous measurements at a smaller number of measurement points, and to visit more points on a seasonal basis, both to determine spatial variability and to validate the continuous measurements.
- **Temporal variability at the study site.** For example, young reservoirs are expected to vary more than mature reservoirs. Continuous measurements should thus be favoured over field surveys in young reservoirs, at least during the initial years after impoundment.
- **Spatial variability across the study site.** Continuous measurements cannot be done at a large number of stations because of maintenance and cost constraints. So if the study site is homogeneous, continuous measurement can be done at a few selected representative stations.
- **When field surveys are the only option left, timing is important and must capture temporal (diurnal, seasonal and annual) variability.** In each case, the extent of variation must be assessed, and then the sampling interval adjusted based on a cost-benefit analysis.
 - Annual variation is affected by study site age, climate (e.g., El Niño and climate change), land-use changes, including city expansions, extreme events (e.g., fires) and disease/pest outbreaks. Fires and disease/pest outbreaks will affect the terrestrial ecosystem directly but also affect the aquatic ecosystem indirectly through leakage.
 - Seasonal variation is affected by temperature, hydrology/precipitation and drought. The number of field surveys per year will depend on seasonal variations specific to each region. In general, there should be from two (wet and dry seasons) to four (winter, spring, summer and autumn).
 - Nycthemeral variation (spanning day and night) is affected by light intensity, temperature and weather conditions (extreme event dynamics such as cold fronts can be important).

3.2.4.1. Terrestrial ecosystems

Emissions and carbon and nitrogen stocks (primary production and decomposition) from terrestrial ecosystems will vary with light intensity, precipitation patterns (amount) and temperature. Extreme events such as insect outbreak, fire, heavy rain and drought can affect the terrestrial ecosystem dynamics, and subsequently that of the aquatic ecosystem via run-off. Both soil- and land-cover GHG flux measurements may be automated to provide continuous monitoring. If that is impossible, diurnal, seasonal and annual variations must be determined by a set number of field campaigns.

3.2.4.2. Aquatic ecosystems

Depending on the reservoir's age, the site's complexity and the resources available, a different frequency of measurements may be used at each site. The short-term dynamics of GHG emissions may be important and it may be necessary to consider semi-diurnal stratification processes to provide more accurate gas measurements. Ideally, variables should be measured automatically at fixed intervals (e.g., every three hours) during the day to account for diurnal variations. If that is impossible, nycthemeral variations should be determined and a correction factor then applied to measurements.

During the initial years of monitoring, younger reservoirs need more frequent measurements than mature reservoirs. If there are major seasonal variations, at least four measurement campaigns are needed every year, but monthly monitoring of key variables and GHG fluxes is likely to be needed to capture seasonal variations and to provide robust mass balance measurements. Key variations in climatic and local conditions should be recorded to determine the sampling frequency and strategy.

The seasonal variation of the fluxes of the entire reservoir system (including the reservoir and river upstream and downstream) must be studied to accurately estimate reservoir emissions. Emissions may vary by more than one order of magnitude during the year due to seasonal variations in organic carbon supply, age, thermal stratification, irregular convective mixing, depth and reservoir operations. Also, significant variations from one year to another have been observed. Statistical analysis should be applied to see whether monitoring results in successive years are similar. If so, future monitoring can be less frequent. If not, annual monitoring should continue until a steady

state is reached. New reservoirs with high gross emissions may need longer periods of emission measurements than mature reservoirs.

3.2.5. Considerations for young and mature reservoirs

Young reservoirs are more prone to spatial variation due to their heterogeneous flooded area (vegetation and soil types). For example, flooded peatlands usually emit more than flooded lakes, rivers or forests in the first year after impoundment (*Blais et al., 2007*). This variation disappears as the reservoir ages (*Bastien et al, 2007*). Hence, more spatially distributed stations are needed to account for spatial variability in young reservoirs. More frequent field surveys are also needed to account for the initial increase and decrease in emissions after impoundment. Measurements in older reservoirs are not critical because if, for any reason, monitoring cannot be performed one year, it can the next with no major loss in information. This is not true for young reservoirs. Priority should always be given to monitoring young reservoirs first.

The period of high initial GHG emissions characteristic of young reservoirs will vary in length (one to five years or more) depending on the quantity and type (lability and carbon content) of flooded vegetation and soil.

3.2.6. Considerations for anthropogenic inputs

Anthropogenic inputs to the river/reservoir should be monitored before and after impoundment to determine the reservoir's effect on them. Spatial and temporal resolution of the inputs is also crucial and presumably different from in the natural aquatic and terrestrial ecosystems. Anthropogenic inputs can affect the carbon and nutrient load to the aquatic ecosystem and its products. Anthropogenic activities affecting the carbon and nutrient load include agricultural (animal manure, land use, farming cycles – ploughing, seeding, etc), urban (waste water and sewage treatment) or industrial (combustion, or nitric acid production) activities. Anthropogenic activities are the main factor affecting N₂O emissions in boreal and temperate ecosystems. In tropical ecosystems, soils rich in ammonium (NH₄⁺) or nitrates (NO₃⁻) are another factor.

3.3. Terrestrial system methodologies

The terrestrial component includes forests, peatlands, marshes and swamps. Marshes, swamps and peatland pools or ponds are at the limit between the terrestrial and aquatic ecosystems. The drawdown zone of reservoirs may be considered as a terrestrial or aquatic ecosystem depending on the water level. Marshes, swamps, peatland pools or ponds, and the drawdown zone of reservoirs may be studied and analysed using both terrestrial and aquatic variables and methods.

Measurement methods are discussed below under two separate headings: GHG emissions and carbon and nitrogen stock. GHG emissions in the terrestrial environment represent fluxes between the atmosphere and soils plus land cover. GHG emission methods use direct flux measurements. Carbon and nitrogen stock variables are used to understand changes, and sometimes to estimate GHG emissions (indirect flux).

3.3.1. GHG emissions

GHG emissions in terrestrial environments are dominated by CO_2 , CH_4 and N_2O . CO_2 fluxes are expressed by the net ecosystem exchange (NEE), which represents the balance between CO_2 uptake through photosynthesis and release through respiration at a given moment in time. Net ecosystem productivity (NEP) represents the annual carbon stock change for a specific location, and includes CH_4 fluxes, loss of carbon from forest fires, and insect outbreaks, as well as dissolved organic carbon (DOC) export.

3.3.1.1. Soil emissions – soil incubation

Soil emissions can be estimated by the soil incubation method. Two variants of the method can be used: air incubation, which estimates emissions in terrestrial environments, or water incubation, which estimates emissions in flooded environments.

The incubation method is used to estimate GHG emissions from specific soil types under predefined conditions. Soil samples are collected from the study area and taken to the laboratory, where they are prepared according to the type of incubation to be performed, and then placed in incubators under controlled temperature or moisture conditions, or both. Temperature-controlled rooms or incubators are needed for this test. GHG emissions are measured by putting the incubated soil sample in a sealed container from which air samples are drawn over a given period of time. Samples are analysed on a gas chromatograph for CO_2 , CH_4 and N_2O concentration, and flux is calculated as the change in concentration over time.

3.3.1.1.1. Soil collection

A number of methods may be used to collect soil samples. The method selected depends on the type of soil (e.g., forest soil or peat) and on specific soil characteristics (e.g., grain size and root biomass). The number of samples and types of soil to be collected depends on the study area.

There are two methods for collecting soil samples in forest ecosystems: the square template and soil core methods. Generally, after removing the plant layer, the organic layer sample is collected using a knife and square template. The template, made of wood, plastic or metal, is placed on the forest floor and the organic layer is sliced free using the knife inside the template. In mineral soil, a steel pipe or soil corer (Figure 3.11) of known diameter (e.g., 5 cm) is driven into the soil to a known depth (e.g., 20 cm). In peat, samples are collected using a box corer (Figure 3.12), which allows simultaneous collection of both oxic and anoxic peat. The collected samples are placed in a sealed container, labelled and taken to the lab where they are kept in a refrigerator or a cold room at 4°C until prepared for incubation.



Figure 3.11: Soil cores

Source: Macaulay Soils

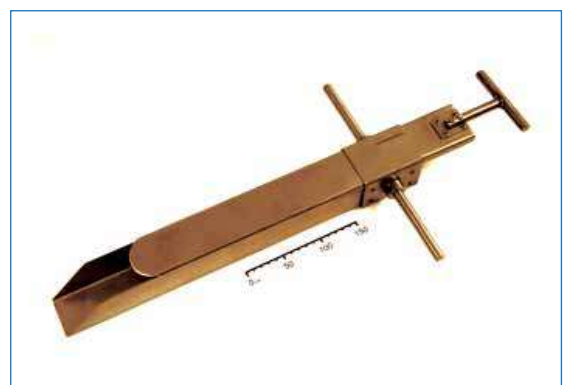


Figure 3.12: Box corer

Source: Macaulay Soils

3.3.1.1.2. Soil preparation

Forest soil samples need preparing before incubation but this should be kept to a minimum to prevent unwanted mineralisation before incubation. For each layer collected, all soil sample replicates from the same sampling site are mixed to get one sample per sample plot. Organic and mineral soil samples are sieved to remove roots, bark and stones, and to make the material homogeneous (Paré *et al.*, 2006). Live sphagnum, wood debris and roots must be removed from peat samples. Due to the disturbance of the soil in the preparation, the exchange rates measured may deviate significantly from in-situ rates and should be regarded as potential rates given the specific experimental conditions.

3.3.1.1.3. Air incubation

The air incubation method may be used to measure the release of GHGs through soil decomposition before reservoir impoundment. Temperature and moisture conditions during incubation should be representative of field conditions where samples were collected.

A predetermined amount of soil (volume and weight) is placed in a container with a plastic mesh bottom. Paré *et al.* (2006) used 25 g of organic soil and 100 g of mineral soil in 150 ml containers. Soil samples are moistened until saturated and left to drain for 24 hours. The containers are then placed in an incubator or growth chamber under predefined temperature and moisture conditions.

GHG emissions may be measured 48 hours after the soil samples have been placed in the incubator. Measurements are made by taking the plastic container and its soil sample and placing it in a glass container with a metal lid (Masson jar) fitted with a septum. Once the glass jar is closed, gas samples are drawn from the headspace through the septum using a syringe fitted with a needle. Samples are analysed on a gas chromatograph. Flux is calculated as the change in concentration over time.

3.3.1.1.4. Water incubation

This type of incubation simulates soil flooded after reservoir impoundment and is used to measure potential GHG emissions. Temperature and oxygen levels during incubation should be representative of reservoir conditions.

A predetermined amount of soil (volume and weight) is placed in a container. Thérien and Morrison (2005) used cylindrical quartz containers 300 mm in diameter and 300 mm in height for

incubation. The container lid must be equipped with a septum for collecting gases and a tube connected to an O₂ cylinder to oxygenate the water column and thus simulate oxic conditions. For anoxic tests, O₂ must be flushed from the water and headspace of the container with nitrogen (N₂).

At the start of the test, the container is filled with a known volume of water from the river or lake to be dammed, leaving a headspace for gas to accumulate. It is important to monitor the water temperature, oxygen level and pH during the test. Flux can be calculated by measuring gas concentrations in the headspace and regressing them over the incubation time.

3.3.1.2. Soil/low-vegetation emissions

3.3.1.2.1. Chamber technique

The chamber technique is the most commonly used method of measuring gas exchange between soil/low vegetation and the atmosphere. Basically, the method consists in placing an open-bottom chamber on the soil surface and measuring the change in GHG concentration over time (Weishampel and Kolka, 2008).

Different chamber designs (steady-state and non-steady-state) may be used to measure fluxes from soil and vegetation. This section will focus on non-steady-state (NSS) chamber design, since most measurements from forest soils, agricultural systems and peatlands presented in the literature use this type of chamber. There are also many advantages in using this design: it is easy to build, the deployment time for flux measurements is shorter and low exchange rates may be measured.

Chamber shape and size, and material used, will depend on the type of measurement to be made, height of vegetation and expected flux rates. The chamber design should be optimised for study-site characteristics. If the chamber is too large, the rate of change in gas concentration will be small, and deployment time longer. If the chamber is too small, it may not be suitable for all heights of vegetation and the smaller area covered by the chamber may not adequately capture the spatial variability. Site accessibility and equipment transport constraints must also be considered: larger chambers can be difficult to carry around.

Flux measurements of CO₂, CH₄ and N₂O can be performed over a period ranging from 2 to 90 minutes or more. The flux measurement period must be established based on the chamber volume and the intensity of the respective fluxes. Low

fluxes will require a longer measurement period to reach a good resolution. In the case of CO₂ (NEE) measurements, flux rate should be looked at carefully before deciding on the length of measurement periods. When measuring photosynthesis by surface vegetation, CO₂ concentration inside the chamber generally decreases over time. If the measurement period is too long, vegetation in the chamber is stressed because of the low CO₂ concentration in the chamber. This can result in a variation in flux rate over time, compared to the initial rate when starting measurements. The flux measurement period should cover only the initial stage, since vegetation is then under conditions closer to those in nature.

Ideally, measurement chambers should be fitted with a mixing fan to ensure adequate mixing of gases inside the chamber. Computer fans connected to a small battery outside the chamber are generally used. The size and number of fans should be a function of the volume and shape of the chamber. Tests should be performed before making final design decisions. The air displacement produced by the fan is also very important. It should approximate conditions in the environment where the measurements are to be made, since wind speed may affect the rate of diffusion between the soil and chamber headspace. It is also an important factor when measuring net ecosystem exchange. Plant stomata tend to close when wind speed exceeds a certain level, so excessive wind speed can alter the vegetation's absorption of CO₂ (*de Langre, 2008*).

Chamber flux measurements should be made using specially designed sampling collars or frames (Figure 3.13) permanently installed in the soil where the measurements are to be made. Installing such frames in the soil before measurement (from one

hour beforehand in dry, bare sandy soil to several weeks in advance when roots need to grow back (*Rochette and Bertrand, 2006*) will minimize the effects of disturbing the soil and damaging roots. The frames may be made of plastic or metal, and their shape will depend on the chamber design. Frames must have a groove in which the chamber can be fitted. When filled with water, this groove prevents air leaking between the chamber headspace and the atmosphere. It is also possible to use a rubber gasket and a fastener to clamp the chamber to the frame and ensure an airtight seal. It is important to avoid putting weight on the chamber even though that would help achieve an airtight seal. Pressure on the soil surface may induce the release of soil gases.

Net ecosystem exchange (NEE) of CO₂

NEE from low vegetation can be measured using clear NSS chambers (Figure 3.14). Measurement chambers are made of clear acrylic glass to allow light to enter, and therefore photosynthesis to occur. This type of chamber must be fitted with a cooling system to prevent the temperature increasing inside (Table 3.5), which could affect plant dynamics and related fluxes. Conditions inside the chamber should be kept as close as possible to ambient conditions at the time of measurement. Time of deployment should also be considered as it may be more difficult to control temperature over a long deployment time. NEE is measured by installing the chamber on the collar for a pre-defined period and by measuring CO₂ concentration regularly over that period.

NEE measurements are made under different light intensities or levels of photosynthetically active radiation (PAR), which will affect flux magnitude and direction. Under clear blue skies, vegetation

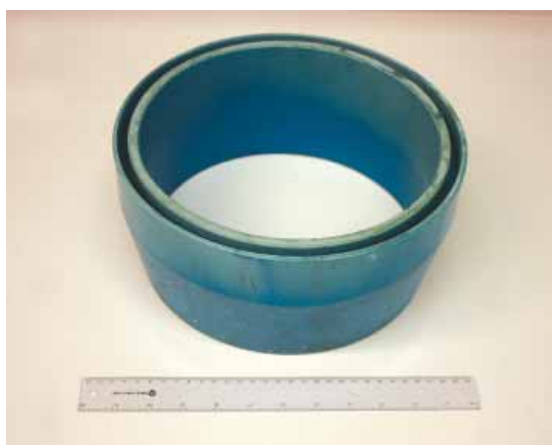


Figure 3.13: Plastic collar used for GHG flux measurements in forests and peatlands (30cm scale)

Source: Université du Québec à Montréal (UQAM)



Figure 3.14: Clear chamber for NEE measurements (30cm scale)

Source: Université du Québec à Montréal (UQAM)

Table 3.5: List of material for NEE (CO₂) measurements

Component	Description
Chamber	Transparent thermoplastic – acrylic glass
Frames or collars	Plastic (e.g., machined blue plastic sewage pipes, see Figure 3.13) or metal
Fan	Computer fan
In/out ports (air)	Swedge lock fittings Polyvinyl chloride tubing 3mm ID (Fisher 14-169-7A)
In/out ports (water-cooling system)	Brass Swagelok tube fitting, Bulkhead Union, 3mm OD tube
Cooling system	Coiled copper tubing, 1.5mm ID, 3mm OD (Cole-Parmer WU-34671-00) Rule 2,000 l/hr bilge pump Small cooler for water and ice
Infrared gas analyser for CO ₂	EGM-4 Environmental Gas Monitor for CO ₂ (PP Systems International, Inc., Massachusetts, USA)
PAR sensor	PAR sensor (PP Systems International, Inc., Massachusetts, USA)

should be absorbing carbon dioxide, so CO₂ concentration in the chamber should be decreasing over the measurement period. At night, the system should be releasing CO₂. Measurement is more difficult in the dark. To get CO₂ measurements under different light levels, shrouds can be installed on the chamber to block part or all of the incoming light (Figure 3.15). These shrouds are made of mosquito netting. One or two layers of netting should block respectively 50% and 75% of the incoming PAR. Dark shrouds made with opaque fabric are used to measure dark respiration (PAR = 0). Measurements under different light levels (no shroud, 50% shroud, 25% shroud and dark shroud) should be made every time the site is visited for NEE measurements. The relationship between NEE and PAR can be obtained by regression of the NEE flux value with the corresponding PAR measured inside the chamber at the time of measurement. The result is an NEE PAR or light response curve. The equation for this curve may later be used to model the fluxes over a longer period if continuous measurement of PAR is recorded.

CH₄ and N₂O fluxes

Chambers for CH₄ and N₂O flux measurements are generally made of acrylic plastic. Chambers must be opaque. Open-bottom 18L water bottles have been used in various studies (Figure 3.6). The chambers are covered with tin foil or thermal aluminium foil bubble insulation to prevent temperature increase inside (Table 3.6).

In order not to disturb the release of gases by inducing pressure on the soil near the chamber, it is recommended that wooden planks are installed in the area of the sampling sites. Samples may also be taken from the chambers through a 2m tube with a three-way stopcock attached to the chamber. If the chamber lacks a fan, the air in the chamber headspace can be mixed before sampling using a 60ml syringe. This would also ensure that the air in the 2m tube is representative of that in the chamber headspace. The air samples may be collected in crimped pre-evacuated glass vials and analysed later on a gas chromatograph, accounting for the evaluation efficiency and the sample dilution of the residual gas in the vials.

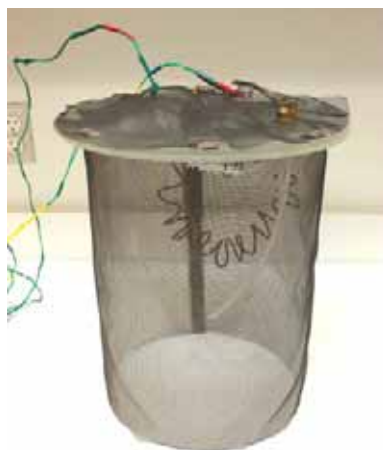


Figure 3.15: Chamber for NEE measurements covered with a shroud

Source: Université du Québec à Montréal (UQAM)

Table 3.6: List of material for CH₄ and N₂O measurements

Component	Description
Chamber	Transparent thermoplastic – acrylic glass or 18L open-bottom water bottle Tin foil or thermal aluminium foil bubble insulation
Frames or collars	Plastic (e.g., machined blue plastic sewage pipes, see Figure 3.13) or metal
Fan	Computer fan
Port (air)	Septum or rubber stopper with 1 hole, size 10 (18L water bottle chamber) Polyvinyl chloride tubing, 5mm ID (Fisher 14-169-7b)

**Figure 3.16: CH₄ and N₂O flux measurement chamber made from an open-bottom 18L water bottle**

Source: Université du Québec à Montréal (UQAM)

Gas analysis

Gas can be analysed by gas chromatography or infrared gas analysers (see section 5). For CO₂, the use of a portable infrared CO₂ analyser is strongly recommended as it provides instantaneous CO₂ concentrations and is cheaper than a CH₄ analyser (appendix 3.2).

Environmental measurements required for annual modelling

Annual GHG exchanges between terrestrial ecosystems and the atmosphere cannot be evaluated just by looking at gas exchanges measured inside chambers. Those measurements give snapshots, so extrapolation is needed to get a value for long periods of time. Fluxes generally correlate well with environmental controls such as light intensity and soil temperature. Annual fluxes of GHGs can be estimated by modelling flux emissions using the relationships observed between the measured fluxes and the environmental controls.

Soil temperature

Increasing the soil temperature normally accelerates decomposition, which increases fluxes at the soil-atmosphere interface. Soil temperature is best measured where flux measurements are taken. Hourly temperature readings at different depths (depending on soil type and physical characteristics) over the entire study period would be ideal. Measured GHG fluxes may later be regressed against soil temperature at the time of flux measurement. The relationship that provides the best coefficient of determination (r^2) should be identified. Its equation should then be used to model fluxes for the study period.

Different equipment setups can be used to measure soil temperature: data loggers can be fitted with air/water/soil temperature sensors or with insulated thermocouples. The latter option is more expensive and requires a sealed enclosure and a 12-V battery.

Photosynthetically active radiation (PAR)

Photosynthetically active radiation (PAR) is the main control on CO₂-NEE. If GHG measurements are made in an open area, PAR measurements from meteorological towers would work. If fluxes are made under a canopy, a PAR sensor should be installed where the fluxes are measured. As for temperature, the hourly average PAR over the entire study period would be ideal. PAR can be measured with net radiometers (Hollinger, 2008).

Soil moisture

Soil moisture should be measured at several depths with a moisture probe. Measurements are recommended at least near the surface (5-10 cm) and at mid-profile (50 cm) depths (Hollinger, 2008). A lot of moisture probes include integral temperature sensors (Hollinger, 2008).

3.3.1.2.2. Eddy covariance tripods

Eddy covariance measurements can be performed using tripods installed in low vegetation areas such as grasslands or peatlands. Eddy covariance is treated in section 3.3.1.3.2 on direct measurements from land cover.

3.3.1.3. Land cover emissions

Indirect measurements of land cover emissions are based on net ecosystem production (NEP) estimates using measurements of the most important biological processes, while direct measurements of land cover emissions are based on net ecosystem exchange (NEE) estimates using eddy covariance or micrometeorology. NEP and NEE are equivalent terms that refer to the balance between uptake and release. However, NEP values usually have a positive sign to refer to accumulation of carbon by the system (the biologist's standpoint) while NEE values usually have a negative sign to refer to absorption of carbon from the atmosphere (the meteorologist's standpoint).

3.3.1.3.1. Indirect net ecosystem production (NEP) measurements

Indirect NEP estimation requires many types of measurements to cover all biological processes involved and is thus fraught with possible manipulation errors. Furthermore, it is practically impossible to measure all biological processes involved. Direct measurement of NEE should thus be preferred over indirect measurement, unless NEP (net primary production and decomposition) values are available in the literature. Regardless of this, a good review of measurement methods for forest carbon monitoring is given in *Field Measurements for Forest Carbon Monitoring* (Hoover, 2008). The main processes to monitor and the names of frequently used methods are given below for information purposes without expanding on each.

Determining net primary production (NPP)

NPP estimates may be obtained from the literature or from a combination of measurements and allometric equations.

Available data from literature

NPP data from various vegetation types can be obtained from the literature (mainly governmental or national sources). For example, the Oak Ridge National Laboratory's Distributed Active Archive Center (ORNL DAAC) gives free access to NPP measurements from various sites around the world: http://daac.ornl.gov/NPP/npp_home.html

IPCC (2003) also presents aboveground NPP (ANPP) by climate zone. NPP values from the literature may be used to estimate NEP, but information must then be obtained for heterotrophic respiration or decomposition (see below). NPP and NEP also could be obtained from remote sensing data using empirical relationships.

Biometric measurements

NPP can be expressed as the sum of increments in live plant mass and dead plant mass, and increment lost to herbivory:

$$NPP = L + D + H$$

where L is the increment in live plant mass, D is the increment in dead plant mass, and H is the increment lost to herbivory (Curtis *et al.*, 2002).

Increment in live plant mass L : Annual wood increment can be estimated by measuring the change in diameter at breast height (DBH) using band dendrometers (Curtis *et al.*, 2002). The average annual increment in aboveground biomass by broad category and for all continents is also available from IPCC (2003).

Increment in dead plant mass D : Annual production of fine litter (leaves, flowers, fruits, etc.), or litterfall, can be estimated by using baskets placed on the forest floor. Baskets are emptied periodically, and their contents are dried and weighed (Curtis *et al.*, 2002; Bernier *et al.*, 2008). Branchfall can be estimated by a combination of fine litterfall traps, forest floor branchfall traps and line transects for coarse woody debris (Bernier *et al.*, 2008).

Increment lost to herbivory H : Loss of leaf carbon to herbivores is estimated by collecting leaves before abscission and comparing their remaining area to that of undamaged leaves of the same size (Curtis *et al.*, 2002).

Determining heterotrophic respiration (Rh) or decomposition

Decomposition should be measured/estimated in three compartments: dead wood, litter and soil. Soil decomposition is the main contributor to R_h (Curtis *et al.*, 2002).

Decomposition of down dead wood

Key factors affecting decomposition of dead wood are moisture, wood quality (density and chemistry), size (diameter and length), and position (contact with the ground) (Scott and Brown, 2008). The most common methods for measuring the decomposition of dead wood are based on chronosequences of dead-wood samples,

the time series approach, and measurements of rates of dead-wood respiration across a range of decay classes (Scott and Brown, 2008).

Litter decomposition

Litter decomposition rates are controlled by four main factors: temperature, moisture, litter quality and faunal community structure (Karberg *et al.*, 2008). Methods of estimating litter decomposition employ mass balance, litterbags, tethered leaves and the cohort layered screen approach (Karberg *et al.*, 2008).

Soil decomposition

Soil decomposition (respiration by heterotrophs) is equal to total soil respiration minus root respiration (respiration by autotrophs). There are five main sources of CO₂ efflux from soil (total soil respiration): root respiration, rhizomicrobial respiration, decomposition of plant residues, the priming effect induced by root exudation or by addition of plant residues, and basal respiration by microbial decomposition of soil organic matter (Kuzyakov, 2006). Kuzyakov (2006) summarises the methods for partitioning total CO₂ efflux from soil into root-derived CO₂ and soil organic matter (SOC)-derived CO₂ (Figure 3.17). Other methods are then required to distinguish root-derived CO₂ as being either root respiration or rhizomicrobial respiration (Kuzyakov, 2006). For both, isotopic and non-isotopic methods can be used (Kuzyakov, 2006). A review of approaches to estimating respiration by autotrophic and heterotrophic organisms in soil is also given by Kuzyakov and Larionova (2005).

Total soil respiration can be quantified using closed-system chambers, open-system chambers and flux gradient sensors (Bradford and Ryan, 2008). Closed-system chambers are commercially available for soil CO₂ efflux measurements. However, there must be some means of separating root respiration from total soil respiration (see Kuzyakov, 2006, and Kuzyakov and Larionova, 2005), such as with models incorporating soil temperature and moisture (Tang *et al.*, 2005) or by performing direct measurements of rhizosphere respiration (root and rhizomicrobial respiration) with potted plants in the laboratory or with a field root respiration chamber (Kutsch *et al.*, 2001).

Calculating net ecosystem production (NEP)

NEP is the difference between NPP and Rh:

$$NEP = NPP - (Rh_{D-W} + Rh_L + Rh_S)$$

Where Rh_{D-W} is heterotrophic respiration from dead wood, Rh_L is heterotrophic respiration from litter, and Rh_S is heterotrophic respiration from soil.

3.3.1.3.2. Direct net ecosystem exchange (NEE) measurements – eddy covariance towers

Direct NEE measurements are made using micrometeorological techniques. These techniques can provide direct, continuous, large-spatial-scale measurements of NEE. The current standard in ecosystem-scale trace gas measurement is eddy covariance (EC). A global network of tower flux stations has arisen in the past few decades and continues to expand into more remote regions and less accessible ecosystems.

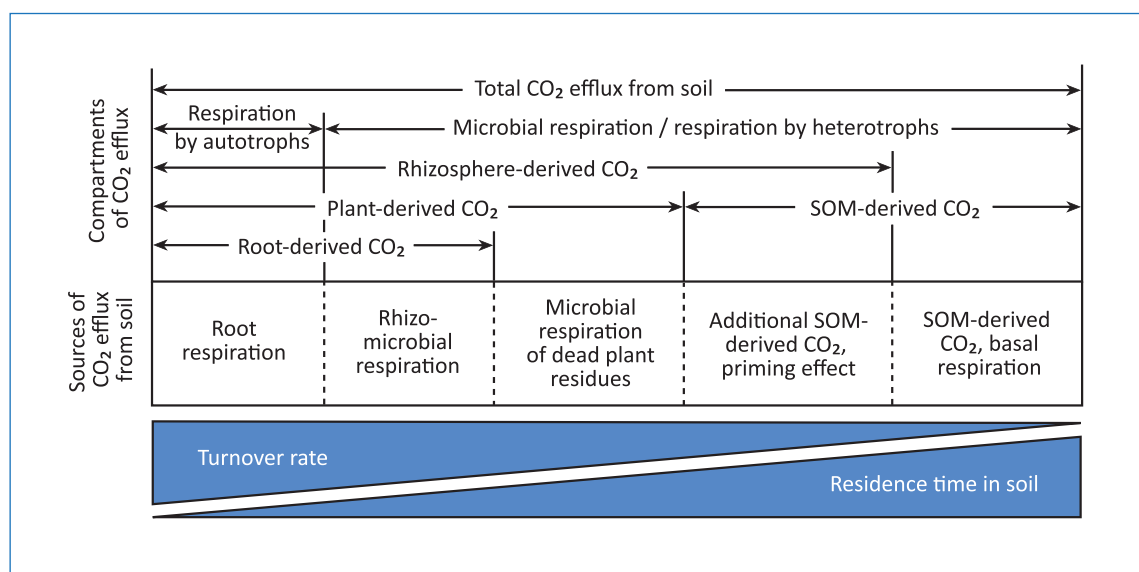


Figure 3.17: Source of CO₂ efflux from soil

Source: Kuzyakov, 2006

The eddy covariance method is the only flux measurement technique that allows direct measurement of the net ecosystem exchange (NEE) of CO₂, i.e., the net vertical flux of CO₂ over a given ecosystem (Baldocchi, 2003). Atmospheric scientists typically use the meteorological sign convention, where negative NEE values represent a net uptake of CO₂ by the ecosystem, and positive values indicate a net release into the atmosphere. NEE relies on the movement of the atmosphere where individual turbulent eddies transport different scalars (CO₂, H₂O) away from and towards the surface. The net ecosystem exchange can be decomposed into the sum of a turbulent component, a storage component and an advective component.

In the atmosphere, turbulence occurs across a frequency spectrum. To measure the rapid fluctuations in concentrations and wind speeds, fast-response sensors are used and measurements are commonly recorded at 10 or 20 Hz (i.e., ten or 20 measurements per second). Measurements are then averaged, typically over a 30 minute period, which captures all turbulent fluctuations (operating at frequencies of less than 30 minutes), while excluding the influence of longer time-scale phenomena (weather patterns). Using the high-frequency data, the turbulent vertical flux of CO₂ (F_c), for instance, is obtained by the covariance between the instantaneous departure (w') from the mean vertical wind speed with the instantaneous departure (C') from the mean gas concentration as:

$$F_c = \overline{\rho w' C'}$$

where ρ is air density and the overbar indicates a time average.

The storage flux (F_s), i.e., the rate of change in storage of CO₂ in the column of air below the instrumentation height, can be calculated based on Morgenstern et al. (2004) as

$$F_s = h_m \overline{\rho_a} (\Delta \overline{S_c} / \Delta t)$$

where h_m is the measurement height, $\overline{\rho_a}$ is the mean molar density of dry air, and $\overline{S_c}$ is the mean CO₂ mole mixing ratio. $\Delta \overline{S_c}$ is the difference between S_c of the subsequent and previous half-hours.

The use of eddy covariance relies on several assumptions to ensure that what is measured represents adequately the surface of interest: the tower must be installed over a flat, uniform surface so that the average vertical wind speed

is zero and flow divergence or convergence is negligible (thus making it possible to ignore the advective component, which is difficult to measure); the flow is fully turbulent so that transport is by turbulent eddies; the upwind edge of the surface of interest (the so-called fetch distance) is sufficiently far away for the boundary layer to have fully adjusted to the surface of interest; and the position of the tower represents the ecosystem of interest for most of the prevailing wind directions. Concerns about the eddy covariance technique in non-flat terrains are pointed out by Araujo et al. (2002), Rocha et al. (2002 and 2004). EC technique encounters severe limitations at night when convection conditions are replaced by stratification. So night-time data must be used with special care.

Use and applications

The main instruments used in EC are the three-dimensional sonic anemometer, which measures wind speed along three axes (the mean flow direction, perpendicular to the mean flow, and vertically), and an infrared gas analyser (both open-path and closed-path IRGAs can be used), which measures the concentration of CO₂ and water vapour. A fast-response thermocouple is often added for the measurement of sensible heat flux, though this term can also be calculated from the temperature fluctuations given by the sonic anemometer. Instruments have now also become available for fast-response measurement of methane concentration. A fast-response data logger is used to operate the system control and data-handling programs. Fluxes are typically calculated in real time and are saved along with the raw high-frequency data on 1 or 2-GB compact flash cards. Depending on the application and sampling frequency, autonomous readings for up to one month are possible.

EC instruments are mounted on the top of tripods (e.g., in peatlands) or on tall towers (e.g., in forests), and oriented toward the dominant wind direction. These systems are supplemented by standard meteorological instruments, which measure, for example, short- and long-wave radiative inputs and outputs, temperature, humidity, precipitation, soil temperature and moisture, and wind speed and direction. Several good reviews of eddy covariance methods, instrumentation and assumptions have been published (e.g., Goulden et al., 1996; Lee et al., 2004; Moncreiff et al., 1996; Pattey et al., 2006).

The EC method's main advantage is that it provides continuous, spatially averaged measurement of the net vertical exchange of carbon, energy and water between the atmosphere and a surface, with minimal disturbance to the environment. As a rule of thumb, it is commonly assumed that the fetch is equal to 100 times the measurement height (h). The source area or flux footprint (i.e. area upwind of the tower that is contributing to the measured fluxes) is then equal to $104 \cdot h^2$. Schmid (1994; 2002) gives good definitions and approaches for calculating source areas.

Data sets enable interpretation and comparison of GHG emission patterns on multiple time scales (hourly, seasonally or annually). EC can also provide information on winter emissions, which are often lacking with other techniques.

Such systems have been used successfully in remote field settings. Typically, power is supplied through deep-cycle marine 12-V batteries that are trickle-charged by a bank of solar cells or a wind generator system. When properly designed and insulated, such power systems run continuously year round, even through harsh northern winters. Where the power supply is an issue, the open-path IRGA is preferred because it does not require a pump so less power is needed. The open-path IRGA is limited in its use to periods without precipitation as the lens must stay clear. Where main power is available, a closed-path IRGA can provide better all-weather data coverage. A cell modem can be used to communicate remotely with the logger. While transfer of the high-frequency data is not yet practical, this remote system check can be useful in deciding when to send staff to the site.

Data processing for EC

With the EC technique, users must perform extra steps as part of the flux calculations, e.g., axis rotation, despiking, detrending, frequency and density corrections. Subsequent data processing includes thorough quality control and gap filling. Since the EC technique relies on turbulent mixing of the air, one EC limitation is that it does not give good measurements during periods of low or intermittent turbulence, such as typically occur during calm nights. Data quality control must be performed to meticulously identify periods when data is not reliable. Such techniques often use a turbulence threshold criterion (e.g., friction velocity) for accepting data. Other tests include spatial representativity and quality control of fluxes, and energy balance closure. As regards

spatial representativity, and knowing that the footprint depends on wind speed and direction, atmosphere stability and surface roughness, it is necessary to check whether the measurements are representative of the plot of interest. Parameterization of Kljun et al (2004) can be used for that. At each time step, distance from the mast and integration of 90% of the sources contributing to the flux is calculated (D_{90}). This distance is then compared to the actual distance to the edge of the plot (D_m). If $D_m < D_{90}$, then the flux is not considered as representative of the plot, and discarded. Note that this method applies only for conditions where turbulence is well established (friction velocity $u^* > 0.2 \text{ m s}^{-1}$). Low turbulence conditions are tested separately in the flux quality controls. These quality controls include tests on the vertical wind speed (with a threshold to avoid too strong correction when performing axis rotations), turbulence intensity, and stationarity.

Following quality control, and after rejection of data due to instrument malfunction and maintenance, gaps commonly occur in the data sets. These gaps may, however, be filled using internationally accepted approaches based on models representing basic ecosystem processes (e.g., *Falge et al., 2001*). Since ecosystem respiration (ER) is mainly driven by temperature, an exponential relationship between night-time NEE and soil temperature is commonly used to model ER for periods when gross ecosystem productivity (GEP) is assumed to be zero, i.e., at night and in the winter. This respiration model is also used to model day-time respiration. Knowing that $NEE = ER - GEP$, it is possible to estimate GEP for the growing season. In terrestrial ecosystems, photosynthetic CO_2 uptake is mostly controlled by photosynthetically active radiation (PAR). The 'measured' GEP values are thus used to build a hyperbolic relationship between GEP and PAR, which allows the modelling of GEP when NEE is missing. The NEE time series can then be reconstructed by subtracting modelled GEP from ER for missing periods. This is why it is essential to continuously monitor meteorological variables. Such ancillary variables are also useful in examining the dominant factors controlling GHG fluxes in response to changes in environmental conditions.

To optimise the use of the EC technique, basic scientific knowledge of the physical properties of the atmosphere is required, along with some statistical background. The processing of EC data is quite complex and requires a significant amount of programming before the flux data can be used in a meaningful way. Most scientists using this

technique use in-house scripts (e.g., Matlab) to perform the different processing steps, but free software packages such as EdiRe (www.geos.ed.ac.uk/abs/research/micromet/EdiRe/) and others are also available and intensively used in the scientific network Fluxnet (<http://daac.ornl.gov/FLUXNET/>), which is the gathering of the different continental networks (Ameriflux, CarboEurop, Asiaflux) measuring NEE across the world. Using this technique also requires regular calibration of the IRGA and maintenance of the systems, so significant person-hours are needed in the field and to process the data.

3.3.2. Carbon and nitrogen stock

The change in GHG emissions is directly affected by the content of flooded organic matter (autochthonous and allochthonous), productivity (affects autochthonous OM) and inputs of allochthonous OM. The evaluation of the carbon and nitrogen stock present in the area to be flooded by the reservoir (and in reference terrestrial sites) is an important measurement, as it can be used as one of the indicators of future reservoir GHG emissions.

Biomass includes aboveground and belowground biomass. This living biomass consumes and produces CO₂ by respiration and photosynthesis, respectively. Biomass gains include total biomass growth from the aboveground and belowground biomass. Losses are caused by decomposition, harvesting, burning or natural disturbances such as insects and diseases. Carbon and nitrogen stock also includes dead organic matter and carbon and nitrogen in forest floor and soils. Dead organic matter comprises dead wood and litter. Carbon from this carbon pool is emitted over years to decades as dead organic matter rots. Decay rates vary between climates and regions.

A good review of measurement methods for forest carbon monitoring is given in *Field Measurements for Forest Carbon Monitoring* (Hoover, 2008).

The sections below outline the compartments where carbon and nitrogen stock should be measured, and mention existing methods. Alternatively, values from the literature can be used to roughly estimate carbon stock from terrestrial environments if empirical data or pre-impoundment measurements are lacking, or to check the order of magnitude of measurements. For example, IPCC (2006) gives information on:

- average aboveground forest biomass by domain, ecological zone and continent (Chapter 4);
- the ratio of belowground biomass to aboveground biomass for forests (Chapter 4);
- average total grassland biomass (above- and belowground) by climate zone (Chapter 6).

Carbon and nitrogen stock from every compartment should be summed to determine the global carbon and nitrogen stock from the terrestrial ecosystem.

3.3.2.1. Aboveground carbon pools

Aboveground carbon pools include biomass in trees, shrubs, grasslands and peatlands, and dead organic matter in forests, peatlands and grasslands. The sections below present specific methods for estimating biomass from each type of vegetation and for estimating dead organic matter above ground.

3.3.2.1.1. Biomass in trees

Biomass in trees can be estimated based on allometric equations using widely accepted forestry variables or on satellite imagery.

Allometric equations and biometric measurements

Aboveground biomass in live and standing dead trees can be estimated by allometric equations relating DBH to bole, branch and stump biomass (Curtis, 2008; Curtis et al., 2002). The total aboveground dry mass of an individual live tree i of species x can be estimated with a typical allometric equation of the form:

$$\hat{M}_{xi} = aD_{xi}^b$$

where D_{xi} is diameter at breast height (1.37 m above the ground), and a and b are parameters obtained from species-specific fitted curves (Curtis, 2008). Plot-level aboveground mass, M_p , can be summed for n individuals of m species:

$$M_p = \sum_{i=1}^n \sum_{x=1}^m \hat{M}_{xi}$$

There are two important points to consider when using allometric equations to estimate biomass (Curtis, 2008):

- Correction factors should be used if allometric parameters a and b were derived from logarithmic regressions. Those correction

factors are usually published along with allometric parameters a and b .

- Selection of the more species- and site-specific equations is critical. Species-specific and general hardwood equations are available in the literature for some parts of the world (*Ter-Mikaelian and Korzukhin, 1997; Jenkins et al., 2003*).

A snag is a standing dead tree with an angle of lean of 45° or less from the vertical (*Curtis, 2008*). Those leaning more than 45° are treated as dead organic matter (see section 3.2.1.5). If the snag is not broken, it can be estimated from the living tree allometric equation as described above. Otherwise, the remaining bole wood volume must be estimated by measuring the snag height (H) with a clinometer, and the area at its base (A_b) and top (A_t) (*Curtis, 2008*). At can be measured from remains found on the ground or estimated visually. Two volume equations can be used, depending on whether the snag volume is estimated as a cone or paraboloid form (*Curtis, 2008*):

$$V = H * (A_b + (A_b * A_t)^{0.5} + A_t) / 3$$

$$V = H * (A_b + A_t) / 2$$

V must be converted to \hat{M}_{xi} using the density of the snag wood, which is function of species and decay class (*Curtis, 2008*). Density data can be found in the literature but snag cores may be needed to determine density on site.

In the field, the following rules should be followed (*USDA, 2006; Curtis, 2008*):

- Data should be collected at the following levels:
 - Plot – data that describe the entire cluster of four subplots (Figure 3.18).
 - Subplot – data that describe a single subplot of a cluster.
 - Condition class – a discrete combination of landscape attributes that describe the environment on all or part of the plot. These attributes include condition class status, reserved status, owner group, forest type, stand size class, regeneration status and tree density.
 - Boundary – an approximate description of the demarcation line between two condition

classes that occur on a single subplot, microplot or macroplot. No boundary is recorded when the demarcation occurs beyond the fixed-radius plots.

- Tree – data describing saplings with a diameter of 2.5 to 12.6 cm, and trees with a diameter of 12.7 cm or more.
- Seedling – data describing trees with a diameter of less than 2.5 cm and a length of 15.2 cm or more (conifers) or 30.5 cm or more (hardwoods).
- Site – tree data describing site index trees.
- All trees in a plot should be tagged with ID numbers.
- Diameter is measured at breast height, 1.37 m above the ground on the uphill side of the tree, or at the root collar for woodland species. The point of measurement should be marked for remeasurement purposes.
- Trees having forked below 1.37 m are treated as separate trees. Other special cases are treated by the USDA (2006).
- The decay class of dead trees should be noted as described in Figure 3.19.

Handbooks on forest ecosystems and forest mensuration may be consulted for more details on allometric equations and biometric measurements. The USDA National Core Field Guide (Appendix 3.1 – Forest Inventory and Analysis National Core Field Guide. Volume 1, Field Data Collection Procedures for Phase 2 Plots) gives valuable information on field data collection.

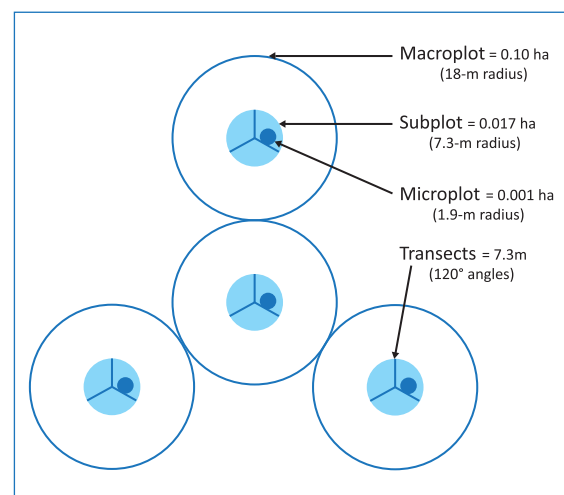


Figure 3.18: Forest sampling plot set-up

Source: *Chojnacky and Milton, 2008*

Decay class stage (code)	Limbs and branches	Top	% Bark Remaining	Sapwood presence and condition*	Heartwood condition*
1	All present	Pointed	100	Intact; sound, incipient decay, hard, original colour	Sound, hard, original colour
2	Few limbs, no fine branches	May be broken	Variable	Sloughing; advanced decay, fibrous, firm to soft, light brown	Sound at base, incipient decay in outer edge of upper bole, hard, light to reddish brown
3	Limb stubs only	Broken	Variable	Sloughing; fibrous, soft, light to reddish brown	Incipient decay at base, advanced decay throughout upper bole, fibrous, hard to firm, reddish brown
4	Few or no stubs	Broken	Variable	Sloughing; cubical, soft, reddish to dark brown	Advanced decay at base, sloughing from upper bole, fibrous to cubical, soft, dark reddish brown
5	None	Broken	Less than 20	Gone	Sloughing, cubical, soft, dark brown, OR fibrous, very soft, dark reddish brown, encased in hardened shell

Figure 3.19: Tree Decay Class

*Characteristics are for Douglas-fir. Dead trees of other species may vary somewhat. Use this only as a guide.

Source: USDA, 2006

Satellite imagery

Spatial and temporal variations in aboveground biomass can be derived from satellite remote sensing data⁴. First, a field-based relationship between the normalised difference vegetation index (NDVI) and aboveground biomass must be established. Based on this relationship, available satellite imagery can then be used to extrapolate biomass to a larger area of similar vegetation. Spectral measurements in each quadrat are sampled with a field spectroradiometer⁵. The NDVI is computed from red and NIR reflectance (Kobayashi and Kato, 2007).

3.3.2.1.2. Biomass in shrubs

A shrub is a woody plant that generally has multiple basal stems growing from the same root system. For this reason, specific biomass methods exist for shrubs, as described in Chojnacky and Milton (2008). Existing methods are described briefly below. In

each method, shrub cover or basal area is measured in the field, and biomass is estimated from those measurements (Chojnacky and Milton, 2008).

Transect intercept cover sampling

The point intercept method records shrub vegetation that intercepts a pole perpendicular to a transect at specified sampling intervals (Chojnacky and Milton, 2008; Figure 3.20):

- Establish the transects from the subplot centre (Figure 3.18).
- Offset the shrub-measurement transects from deadwood transects to minimize site disturbance.
- At each sample point along the transect, record the highest intersection of vegetation hitting the pole. Alternatively, the highest intersection among height classes can be recorded for greater detail.

4 Biomass estimation from satellite, in tropical forests and tropical savannahs, is still far from reliable. So the use of this technique will depend largely on field validation and the desired precision of the estimates.

5 A field spectroradiometer can also be used to obtain the spectral information of different water body and greenhouse gas concentration in atmosphere, chlorophyll a in water and other important parameters. Future editions of this Manual will include details on spectral measurement, including measurement instruments, methods and important notices.

- Vegetation hits can be recorded at species or species group level, depending on the detail desired.

Percent shrub cover is calculated by summing the number of sample points where vegetation intersects, or hits the pole and dividing by the total number of points sampled:

$$\text{cover}_{jk} = \sum_{i=1}^N 100 \frac{P_{ijk}}{N}$$

where cover_{jk} is the percent shrub cover for height j of species or species group k and $P_{ijk} = 1$ if foliage intercepts sample pole at point i for height layer j of species k and $P_{ijk} = 0$ otherwise. N is the total number of points sampled in layer j for all transects on the plot. An equation to convert shrub cover to biomass must then be constructed. Only a few equations exist in the literature.

The line-intercept method is a variant of the previous method that records vegetation cover by measuring the length (horizontal distance) of shrub cover that intersects the transect (Chojnacky and Milton, 2008; Figure 3.21).

Canopy cover sampling

Canopy cover can be estimated visually to the nearest percent or within predetermined cover classes (1%-5%, 6%-10%, 11%-20%, 21%-40%, 41%-60%, 61%-80% and 81%-100%). Canopy cover estimates can be performed within identified (flagged) microplot boundaries using percentage area guides for aiding visual estimation. It is

useful to divide the microplot into four quadrants, estimate each of them separately and then average the results (Chojnacky and Milton, 2008). Two or more people can make independent estimates to reduce subjectivity. A variant of this method adapted for small shrubs consists of estimating canopy cover in small quadrats (1 m² or smaller) spaced along transects radiating from each subplot (Chojnacky and Milton, 2008).

Diameter measurements

In this method, the basal diameter of each shrub in a microplot is measured at the root collar (Chojnacky and Milton, 2008). A minimum diameter should be set to simplify measurements. Shrub stems not included because of their small diameter might be included in herbaceous cover measurements or just ignored given their small incremental value (little carbon content for the field effort required). Total basal area (Y_k) for species k (m²/ha) can be computed as follow:

$$Y_k = \sum_{i=1}^{S_k} \frac{\pi drc_{ik}^2}{40,000 A_{mp}}$$

where drc_{ik} is the diameter near the root collar for stem i of species k (cm), A_{mp} is microplot area (ha) and S_k is the total number of stems for species k measured on the microplot. Biomass can be computed with an appropriate diameter-based regression equation. This method is the most labour-intensive, but more objective in estimating shrub cover biomass.

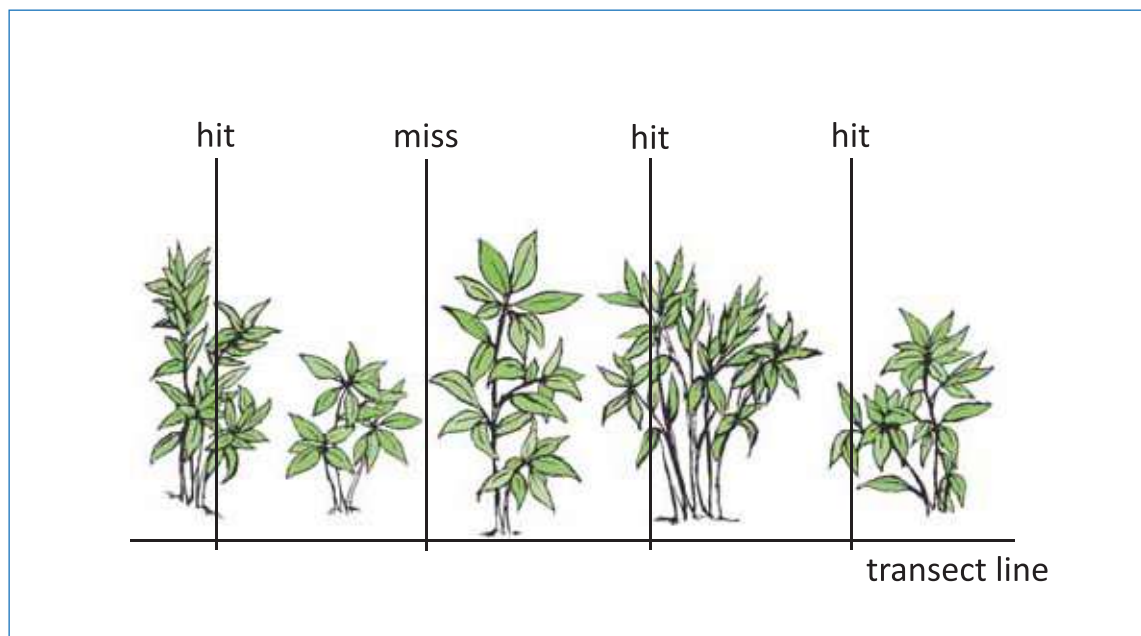


Figure 3.20: Shrub point-intercept method

Source: Chojnacky and Milton, 2008

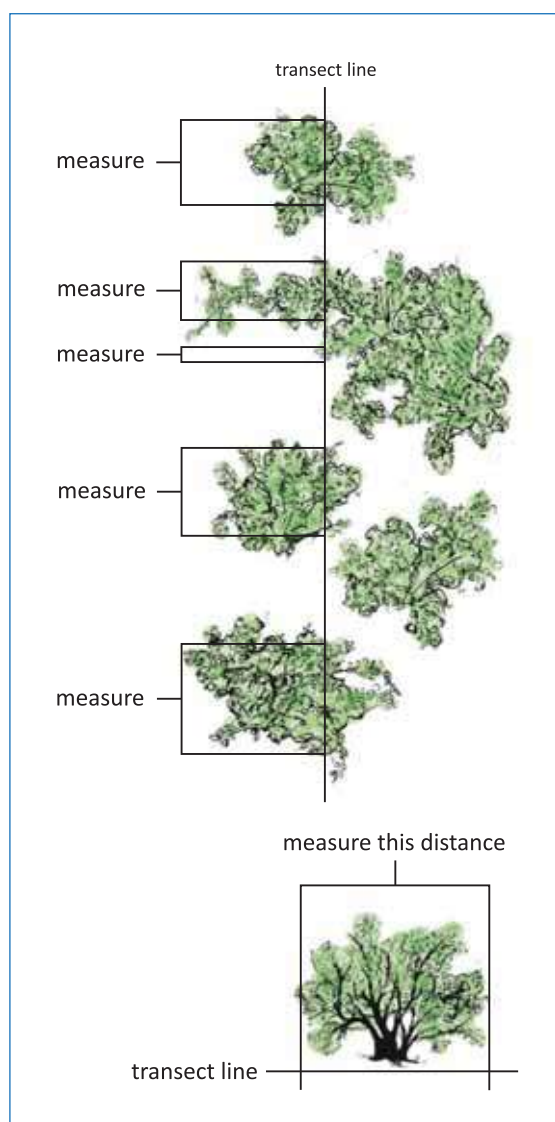


Figure 3.21: Shrub line-intercept method

Source: Chojnacky and Milton, 2008

Regression between cover or basal area and carbon content

To estimate biomass using the methods mentioned above, a regression must be developed between cover or basal area and shrub weights taken from subsamples (Chojnacky and Milton, 2008):

$$biomass_T = \text{Exp}[a \ln(\text{cover}) + b]$$

$$biomass_p = \text{Exp}[a \ln(\text{drc}) + b]$$

where $biomass_T$ is the total shrub dry weight (Mg/ha) and $biomass_p$ is individual shrub stem or plant dry weight (kg/plant). Biomass can be estimated by various methods such as those proposed and described by Gregoire et al. (1995): randomised branch sampling (RBS), importance sampling (IS) and two-stage (RBS and IS) sampling.

3.3.2.1.3. Biomass in grasslands and peatlands

In the case of areas with low vegetation, such as grasslands and peatlands, it is possible to estimate aboveground biomass by clipping vegetation inside quadrats, sorting it into foliar and woody tissues, oven-drying it at 80°C over 24 to 48 hours and weighing it (Bubier et al., 2006). Belowground biomass can be determined by excavating quadrats, sorting living biomass from dead organic matter, oven-drying it at 80°C over 24 to 48 hours and weighing it (Moore et al., 2002).

3.3.2.1.4. Dead organic matter in peatlands and grasslands

In peatlands, dead organic matter can be determined by excavating quadrats, sorting dead organic matter from living biomass, oven-drying it at 80°C over 24 to 48 hours and weighing it (Moore et al., 2002).

3.3.2.1.5. Dead organic matter in forests

In forests, dead organic matter comprises coarse woody debris and logs. The most popular methods for estimating dead organic matter in logs are line intersect sampling, plot relascope sampling, plot relascope sampling, the prism sweep, and perpendicular distance sampling (Valentine et al., 2008). Methods vary in that the probability of a log being included when sampling may depend on its length or volume. Ideally, probability of inclusion should depend on volume since this variable is directly linked to the carbon content. This is true with perpendicular distance sampling (Valentine et al., 2008):

- Select sample points using a systematic grid.
- Identify the log's inclusion zone which is proportional to the log's volume (Figure 3.22, left).
- Measure the perpendicular distance, D , from the log (including branches) to the sampling point. The log is selected if $D \leq K_v a$ where a is the cross-sectional area of the log at the point of intersection with the perpendicular line, and K_v is a constant fixed by the user (Figure 3.22).
- Calculations are described by Valentine et al. (2008).

3.3.2.2. Belowground carbon and nitrogen pools

Belowground carbon and nitrogen pools include the forest floor (organic horizons), the mineral soil carbon content (mineral horizons), and root biomass (Burton and Pregitzer, 2008). Soil carbon stocks are one of the largest carbon pools in forest and wildland ecosystems (Burton and Pregitzer,

2008). Coarse root biomass can also be a large pool with typical values of around 20% to 30% of the aboveground carbon content in wood (*Burton and Pregitzer, 2008*).

Soil classification may be needed to identify the type of horizons likely to be found in the project area. Classification typically distinguishes the organic (L, F, H) and mineral (A, B, C) horizons. Soils are a mixture of organic and inorganic constituents that are in solid, gaseous and aqueous states. The soil lies below the litter and has a smaller particle size. Organic soils (peat and muck) have at least 12% to 20% of organic matter by mass, whereas all other soils are considered mineral soils (*IPCC, 2006*).

3.3.2.2.1. Carbon and nitrogen in forest floors

Forest floors can be sampled using 30- x 30-cm frames, separating material from each organic horizon, drying it at 70°C for 48 hours, then weighing and grinding it before analysis for elemental carbon (*Burton and Pregitzer, 2008*).

3.3.2.2.2. Carbon and nitrogen in mineral soil

Mineral soil carbon content can be obtained using volumetric pits or core sampling to a depth of at least 30 cm for annual vegetation, and 60 cm or more for perennial vegetation (*Ellert et al., 2008; Burton and Pregitzer, 2008*). Beneath 70 cm, additional samples for soil carbon and nitrogen analysis may be obtained using soil augers (*Burton and Pregitzer, 2008*). As a general rule samples should be collected to a depth of 50 cm and taken at incremental depths (for example: 0-10 cm, 20-30 cm and 40-50 cm).

- a. QA/QC procedures should include the following steps (*Burton and Pregitzer, 2008; MDDEP, 2008*):
 - Wash and brush the sampling instruments, e.g., shovel, corer, auger or tube (Figure 3.23), with water, acetone, ethanol (alternatively, hexane, although riskier to health) and again with acetone, in that order, to prevent contamination of soil samples. Instruments should be washed between each sampling site and each depth increment. Washing liquids should be recovered and disposed of in an appropriate place. Instruments may be wrapped in aluminium foil between washing and sampling.
 - Perform mineral soil carbon content sampling first and then forest floor sampling at the same sites to avoid mixing litter or organic horizons with the mineral horizons.
 - Widen pits between depth increments (Figure 3.24).
 - Mix samples from each depth separately to obtain a homogeneous mixture. If the soil contains large particles (> 2 mm), sieve it to collect only the fine portion, which is more subject to bacterial degradation.
 - Fill glass bottles (250 ml) with soil using a spoon or spatula. Do not leave any free space. The laboratory usually supplies pre-washed glass bottles.
 - Take 10% of the samples in duplicate.

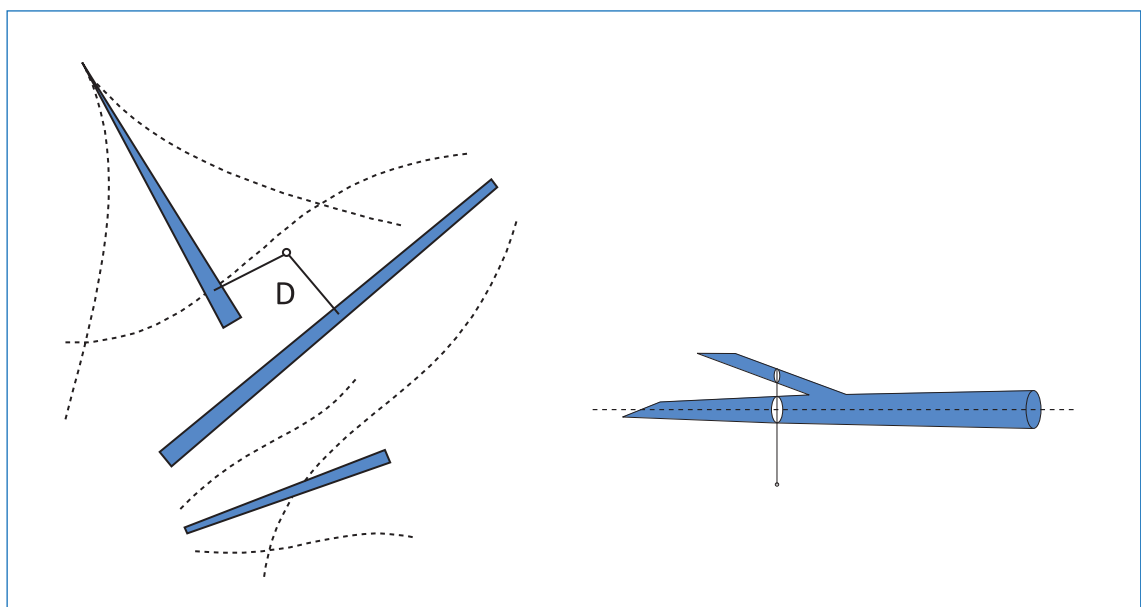


Figure 3.22: Log perpendicular distance sampling method – area of inclusion (left) and cross-sectional areas (right)

Source: *Valentine et al., 2008*

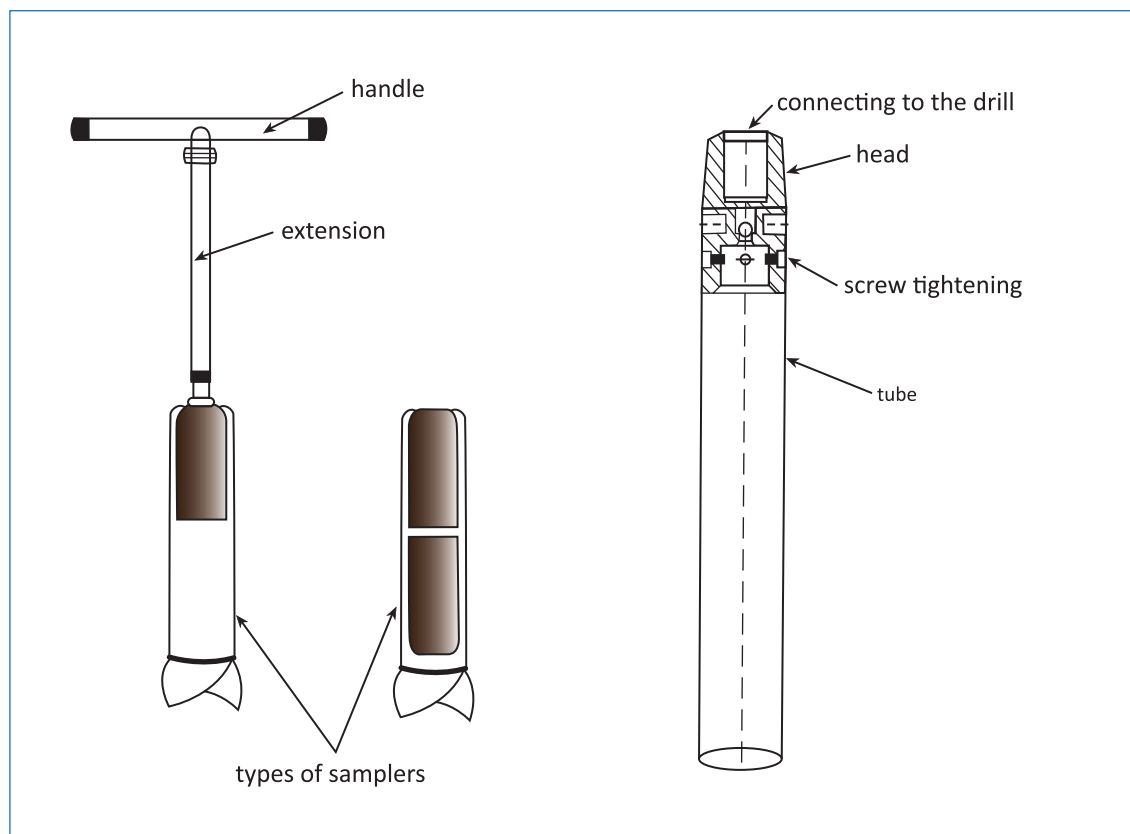


Figure 3.23: Auger (left) and tube (right) for soil sampling

Source: MDDEP, 2008

- Keep samples at 4°C in the dark before analysis.
 - Send samples to a specialised lab. Alternatively, soil samples may be prepared and analysed using a TIC/TOC analyser as described in section 3.4.2.3.
- b.** Determine the sample's volume using the water method or foam method. The water method consists of placing a plastic bag in the core hole and recording the volume of water needed to fill the hole. Determining volume by the foam method involves the following steps:
- Insert markers at each depth increment (pit should not have been widened).
 - Fill the entire core hole with polyurethane foam, place a cardboard cover and weight to seal the surface, and wait eight hours to let the foam expand and fill irregularities.
 - In the laboratory, foam casts are cut into segments corresponding to depth increments and sprayed with water-resistant clear-gloss urethane to create a waterproof seal.
 - The volume for each depth increment is determined by water displacement.

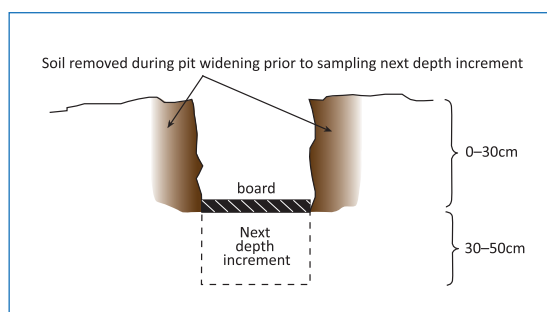


Figure 3.24: Pit widening between soil depth increment sampling

Source: Burton and Pregitzer, 2008

Separate the stone and soil fractions, and determine their density to ensure accurate estimates of carbon and nitrogen stock per unit area (Burton and Pregitzer, 2008; Figure 3.25).

- c.** The volume of stones is determined by their mass (M_{st} > 10 mm and 2-10 mm) divided by their density (D_{st}): $V_{st} = M_{st} / D_{st}$
- The bulk density (D_B) is determined by the total dry mass of all material (stones, organic material, soil < 2 mm, coarse roots and fine roots) in the depth increment divided by the total volume of the depth increment:

$$D_B = M_T / V_T$$

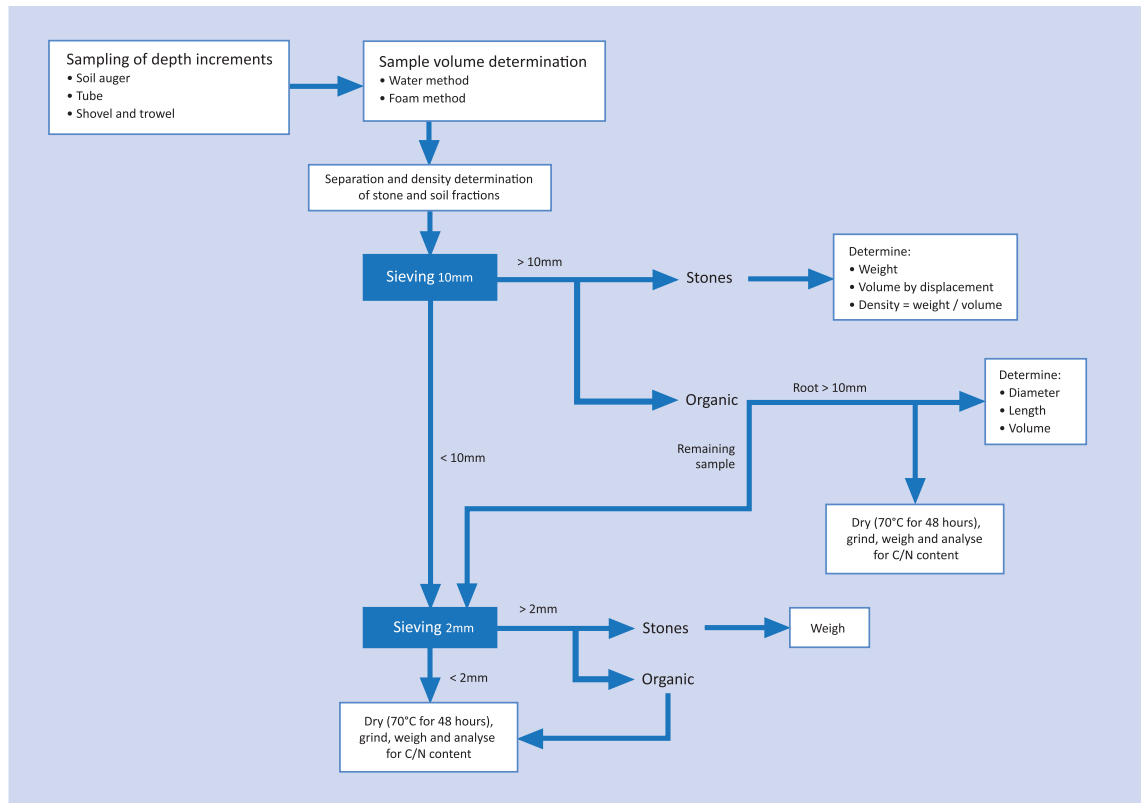


Figure 3.25: Mineral soil sampling

- The volume of the fine fraction (V_F , < 2 mm) is equal to the total volume minus the volume of the stone fraction and the volume of the coarse-root fraction (V_{CR} , > 10 mm in diameter): $V_F = V_T - V_{St} - V_{CR}$.
- The fine fraction density (D_F) is determined by the mass of the fine fraction (M_F) divided by its volume: $D_F = M_F / V_F$.
- Total carbon stock is obtained by adding the carbon stock (S_C) of each depth increment sampled. Calculation of carbon stock for each depth increment is equal to:

$$S_C = \frac{T_I \times [(C_{FS} \times M_{FS}) + (C_{OM} \times M_{OM})]}{V_T}$$

where T_I is the thickness of the depth increment, C_{FS} is the carbon concentration of material passing the 2 mm screen, C_{OM} is the carbon concentration of organic material > 2 mm (other than coarse roots > 10 mm in diameter), M_{FS} is the mass of material passing the 2 mm screen, M_{OM} is the mass of organic material > 2 mm and V_T is the total volume of the depth increment.

- The C:N ratio for each soil fraction should be determined and used as an indicator of biological availability. The nitrogen stock should also be determined.

3.3.2.2.3. Carbon in roots

Destructive methods exist for measuring carbon stored in roots, but they are labour-intensive. Belowground biomass can be derived from allometric equations relating DBH to woody root mass (Burton and Pregitzer, 2008). For most tree species, only general relationships are available, in which belowground wood mass is set at a fixed fraction of aboveground wood mass (Curtis et al., 2002). Alternatively, carbon concentration of all coarse roots may be assumed to be the same as coarse roots sampled in the soil pits (Burton and Pregitzer, 2008; see section 3.3.2.2.2).

3.3.2.2.4. Dissolved organic carbon

Lysimeters are used to collect samples in unsaturated soils, while wells and piezometers are used where water tables are present (Kolka et al., 2008). Lysimeters can be installed between the organic and mineral horizons to determine the flux of carbon between the two, and in or below the mineral horizon to determine the quantity of carbon leaving the ecosystem (Kolka et al., 2008). Filtration using a pore size of $0.45 \mu\text{m}$ is necessary to retrieve particulate organic carbon (Kolka et al., 2008). See section 3.4.2.3 for elemental C analysis.

DOC fluxes can be estimated by multiplying DOC concentration by the water flux. At the watershed level, flow can be measured at a weir or flume (Kolka et al., 2008).

3.3.2.3. Mass-to-carbon conversion

The relation between biomass and carbon is species-specific and tissue-specific: the carbon content of woody mass varies across constituent tissues, such as bark, sapwood and hardwood, depending on tree species (*Curtis, 2008*). A bioassay should be performed to determine the actual relation between biomass and carbon. As a rule of thumb, the carbon content equals 50% of the biomass weight (*Valentine et al., 2008*). Some species-specific relations of biomass to carbon content are presented in chapter 4 of IPCC (2006).

3.3.2.4. Total terrestrial biomass

Biomass measured or estimated from the aboveground (section 3.3.2.1) and belowground (section 3.3.2.2) pools should be summed to gauge the total terrestrial carbon stock. The DOC fraction (section 3.3.2.2.4) of the total carbon stock is important to determine leakage of carbon between terrestrial and aquatic ecosystems.

3.4. Aquatic system methodologies

Similarly to terrestrial ecosystems, aquatic ecosystems in the study site must be characterised before making GHG measurements in order to understand spatial and temporal variations. For instance, information on bathymetry, flow conditions, sediment and changes in water level may provide valuable insights on GHG emissions and carbon and nitrogen stock in aquatic environments.

Measurement methods are discussed separately below for GHG emissions and carbon and nitrogen stock. GHG emissions in the aquatic environment represent fluxes between the atmosphere and water surface (diffusive flux) and bubbling from the sediment to the water surface. In reservoirs, a third emission pathway is possible at weirs, dams and spillways, where rapid change in pressure favours degassing of less soluble gases. Carbon and nitrogen stock variables are used to understand changes in GHG emissions and may also be used as a proxy to estimate GHG emissions.

The International Organization for Standardization (ISO) provides guidance on sampling from lakes, natural and man-made, and on the design of sampling programmes and sampling techniques in aquatic systems (Appendix 3.1).

3.4.1. GHG emissions

CO₂, CH₄ and N₂O are three predominant GHGs emitted naturally by aquatic systems, the first two being the most important.

CO₂ and CH₄ gas concentrations in water can be influenced by several factors, including:

- mixing regime (for example, in boreal ecosystems, autumn and spring turnover transport the water enriched in dissolved gases from the bottom to the top of the water column; or the up/down welling process in tropical reservoirs, associated with wind frequency);
- abundance of algae and plants, and their photosynthetic rates;
- quantity of organic matter entering the system and its decomposition rate in the water column and sediment (CH₄ is produced in anoxic sediment by fermentation (*Wang et al., 1996*));
- water residence time, which affects dissolved organic matter availability;
- dissolved oxygen content, which affects the rate of CH₄ consumption by methanotrophic bacteria (*Wang et al., 1996*).

N₂O emissions vary from up to 30% in some tropical reservoirs (*Guérin et al., 2008*) to less than 1% in boreal reservoirs (*Tremblay et Bastien, 2009; Hendzel et al., 2005*). Levels of N₂O can be increased by the presence of significant inputs of nitrogen from the watershed (see section 2.2.2.3).

3.4.1.1. Diffusive surface flux

3.4.1.1.1. Floating chambers

The floating chamber method is a cheap and convenient method to measure direct diffusive fluxes at the surface of aquatic ecosystems. This method consists of enclosing air in a chamber that floats at the surface of the water (Figure 3.26). Fluxes are then calculated according to the change of the concentration of the gas in the chamber (*Abril et al., 2005; Guérin et al., 2007; Tremblay and Bastien, 2009*).

Diffusive fluxes depend on the concentration gradient between the surface microlayer and the atmosphere and physical variables such as wind speed and rainfall (*Borges et al., 2004 a and b; Guérin et al., 2007*). Artificial turbulence can be created by the chamber itself due to friction between the edges of the chamber and the water. When the chamber walls do not extend below the water surface, the chamber drifts, creating turbulence that can generate gas fluxes up to five times higher than in chambers

with wall extensions into the water (*Matthews et al., 2003*). This becomes important at low wind speed ($\sim 1 \text{ m s}^{-1}$) (*Matthews et al., 2003*). Thus, floating chambers must have walls extending below the waterline (Figure 3.26). In turbulent environments, the chamber can rock back and forth and bob up and down, increasing the turbulence at the air-water interface. The chamber can be stabilised by weights attached to the bottom of the chamber skirt. It is important to stress that generally it is unnecessary to weight the base of the chambers. However, if strong waves are likely, then weighting becomes mandatory. The solubility of gases in water depends on pressure and temperature. When the pressure increases, the solubility increases and vice versa. A vent must be installed on the top of the floating chamber to equalise the air pressure in the chamber with the atmospheric pressure before starting the measurements (Figures 3.26 and 3.27). To limit variation of temperature inside the chamber, the enclosure must be covered with reflective material. Typical dimensions and characteristics are as follows:

- Height above the water surface while floating: 15 cm.
- Chamber walls must extend 2-4 up to 15 cm below the water surface depending on the instability at the site caused by wind, waves, etc.
- Surface: 0.2 m^2 .
- Volume: 30 litres.

As discussed by Kremer et al. (2003), a chamber that moves relative to the surface water would disrupt the aqueous boundary layer and artificially

enhance gas exchange. If fluxes are not measured while floating freely with water movements, there is significant overestimation of the fluxes, since turbulence is artificially enhanced by the friction between the chamber walls and the water. Thus, measurements must be performed while the chamber is drifting with the water at lake and river surfaces. However, in environments with low water current but high wind, it is preferable to anchor the chamber to stop it moving in the wind; in environments with high currents, drifting with water masses is necessary (*Frankignoulle et al., 1996*).

GHG concentration in the chamber can be measured in two ways, either in-line (continuous) using portable gas analysers, or by taking air samples (non-continuous) for gas chromatography analysis in the laboratory. In the continuous approach, concentrations are measured in the field over a given period (seven minutes). In the chromatograph approach, grab samples of air are collected using a series of syringes, thus providing fewer points on the curve of gas concentration over time. Gas samples are analysed by specialised laboratories. The continuous approach may better capture the relation between gas concentration and time, but is probably more expensive due to the cost of the instruments. Both methods are described briefly below.

Continuous approach

- Air in the chamber is sampled from the top of the floating chamber.
- Two openings for the connection of the gas analysers have to be built: air is pumped via the tubing (outlet) through the analytical

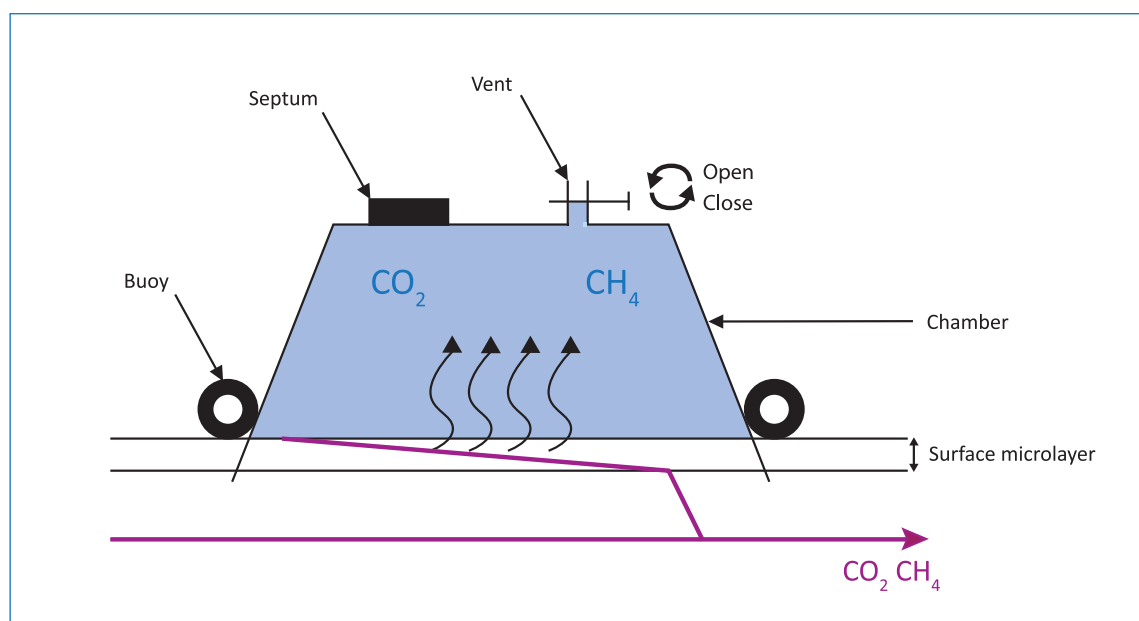


Figure 3.26: Sketch of a chamber design used to measure diffusive surface flux

Source: UNESCO/IHA, 2009



Figure 3.27: Example of chamber design

Source: Environnement Illimité Inc.

Source: SINTEF

instrumentation in a loop that returns to the chamber (inlet). The air flow is determined by the instrument specification and should be constant. A diaphragm pump can be used.

- A desiccant (magnesium perchlorate) is placed at the outlet of the floating chamber and in front of each instrument to prevent condensation in the tubing and damage to certain instruments (see the specifications for each instrument).
- Measurements are made over about a seven-minute period.
- Air is analysed with a portable instrument.
- Data is collected with a data logger or portable computer. All readings (various intervals) are plotted on a graph of gas concentration as a function of time.

Non-continuous approach

- With this approach, there is only one chamber outlet. The chamber can be equipped with a septum (pre-boiled butyl rubber or Viton) to take samples inside the chamber with a syringe equipped with needles.

- Air samples must be taken from the chamber after mixing the chamber air volume by pumping with a syringe.
- A typical syringe will have a sample volume of 60 ml and a two-way valve.
- Gas samples collected may be analysed for CH₄, CO₂ and N₂O using a gas chromatograph (see section 3.5.1). Details on the use of this instrument are given by Keller and Stallard (1994) and by Weiss (1981).
- At least four gas samples (each replicated) should be collected for the regression between time and gas concentration.

The correction for temperature and pressure is assumed to be done automatically by the instruments (*Lambert and Fréchette, 2005*) when using the continuous approach and IRGA. In this case, standard temperature and pressure (STP) values should be used. Otherwise, when using the non-continuous approach and gas chromatography analysis, pressure and temperature corrections have to be made manually by using the measured value in the F1 conversion factor.

Flux calculation

The flux is obtained by calculating the slope of the regression line using the following equation:

$$Flux[mg.m^{-2}.d^{-1}] = \frac{Slope[ppm.s^{-1}] * F1 * F2 * ChamberVolume[m^3]}{ChamberSurface[m^2]}$$

Where F1 is a conversion factor from ppm to mg m⁻³ for standard temperature and pressure (STP) for gas in air (perfect gas formula):

$$GasConc[mg.m^{-3}] = \frac{GasConc.[ppm] * MolecularWeight[g.mole^{-1}] * AtmP[KPa]}{8.3144J.K^{-1}.mole^{-1} * (273.13K + T[°C])}$$

and where F2 is a conversion factor of seconds into days (24 hr * 60 min * 60 s = 86400 s d⁻¹)

Atmospheric pressure

WMO (2008) – No. 8, Part I – Chapter 3: The atmospheric pressure on a given surface is the force per unit area exerted by virtue of the weight of the atmosphere above. For meteorological purposes, atmospheric pressure is generally measured with electronic barometers, mercury barometers, aneroid barometers or hypsometers.

Water temperature

See section 3.4.1.1.3.

3.4.1.1.2. Eddy covariance towers

Micrometeorological methods can be used to determine the turbulent diffusion of trace gases over water surfaces. The eddy covariance method is described in detail in section 3.3.1.3.2, as it has been widely used in terrestrial ecosystems. Current research is extending its use to aquatic systems.

The use of the EC technique for measuring GHG fluxes in aquatic systems is similar to the use for terrestrial systems. However, a few more factors must be considered. Over a large body of water, the flux tower containing the instruments should be installed on a stable platform. A small island can be used, but in that case all data corresponding to wind directions originating from the island must be discarded to avoid contamination of the fluxes from non-water sources. If small bodies of water are to be studied, the effect of nearby non-water surfaces may be significant as the turbulence over heterogeneous ecosystems may influence the measured fluxes (e.g., *Vesala et al., 2006*). EC also provides fluxes of latent and sensible heat directly, which may be interesting for studies on energy and water budgets in aquatic systems.

Gap filling of missing NEE data is more complex for aquatic systems since, unlike terrestrial ecosystems, there are no standard protocols. It should be remembered that the EC technique estimates the flux at the water-air interface. This is unlikely to be the original source of the gas flux itself. Currently, the best way to estimate NEE from missing periods of EC measurements may be based on site-specific relationships. Correlations are likely between the measured CO₂ fluxes from water and some environmental measurements related to the exchange process, such as wind speed.

3.4.1.1.3. Thin boundary layer (TBL)

The TBL method calculates flux using semi-empirical equations. Although a lot of literature exists on this subject, the mechanisms that drive the process remain poorly understood so predictions have large uncertainty. For example,

widely used predictive models of the gas transfer process commonly differ by factors of three or more, and contain poorly understood nonlinearities as noted by Banerjee and MacIntyre (2004). This translates to uncertainties of at least 300% in recent attempts to calculate a net oceanic CO₂ uptake (*Takahashi et al., 2002*). Such uncertainty is due to the highly variable nature of correlating factors, e.g., wind, waves, surfactants, thermal convection or stratification, wave breaking, and upwelling. The local variables necessary for the calculations are the concentration of the GHG in air and in the water, the wind speed, and the water temperature.

It is recommended to use floating chambers connected to a real-time measurement system (if wind and weather conditions allow). This system could be used in both pre- and post-impoundment studies. If real-time measurements are not feasible, measurement campaigns with floating chambers must be done in accordance with spatial and temporal resolution requirements. In the future, TBL might be used more often, but the approach still needs to be tested more.

GHG partial pressure measurements

GHG partial pressure measurements can be performed with an IRGA connected with an air/water exchanger (contactor) or with headspace gas chromatography (HS-GC).

Infrared gas analysers and contactor

GHG partial pressure can be measured with portable gas analysers (see section 5) connected in-line with a contactor (air/water exchanger). The contactor is a plastic cylinder traversed by numerous polypropylene micrometric tubes. The surface water, collected by means of a peristaltic pump, circulates continuously inside



Figure 3.28: Automated system installed on a floating deck (other types of buoys may be used)

Source: Environnement Illimité Inc.

the contactor, in the direction opposite to the air passing through the micrometric tubes that bathe in the sampled water. The gas concentration of air circulating in the micrometric tubes balances with the gas concentration in the water. The resulting gas-enriched air is then analysed.

This system can be used for discrete measurements (field sampling) or can be automated for continuous measurements inside a generating station, or on a floating deck or buoy (Figures 3.28 and 3.29). Automated GHG measurement systems combine a gas analyser with a data logger, contactor, and set of tubing and valves to sample water and air alternately. Continuous measurements may reveal clear seasonal trends in GHG emissions.



Figure 3.29: Automated system installed inside a generating station

Source: Environnement Illimité Inc.

Headspace gas chromatography (HS-GC)

HS-GC is used to estimate GHG concentration in water samples. Figure 3.30 shows the principle of the headspace technique, where the gas phase or headspace lies above the liquid sample phase containing the dissolved gases. Once the sample

phase is introduced into the vial and the vial is sealed, volatile components diffuse into the gas phase until the headspace has reached a state of equilibrium (static HS-GC⁶), as depicted by the arrows. The sample for analysis is then taken from the headspace.

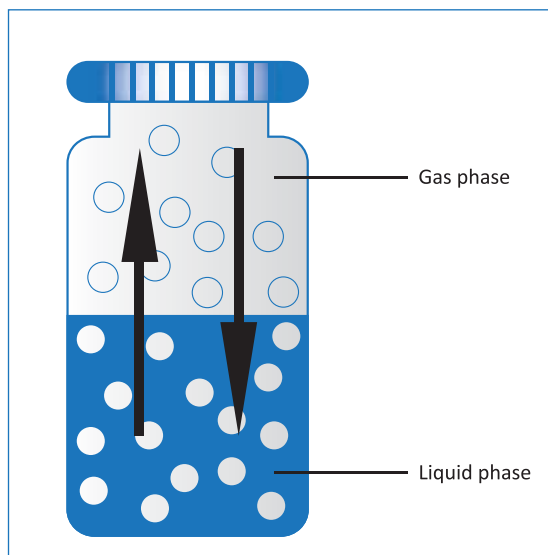


Figure 3.30: Principle of the headspace technique

Source: Modified from Kolb and Ettre, 2006

Collection of water samples

For gas concentration analysis, water samples can be taken at various depths to determine the gas profile at a specific station (e.g., upstream of the dam near the water intake). However, when the goal is to calculate diffusive fluxes, water samples should be collected at the water surface. For gas concentration analysis, water samples can be taken at various depths to determine the gas profile at a specific station (e.g., upstream of the dam, near the water intake). In that case, a gas-tight container should be used to collect water samples (e.g. Kemerrer, Van Dorn or Niskin sampler). Water samplers that allow gas exchange are not appropriate.

The following steps and QA/QC items should be considered when designing the procedure for collecting water samples for HS-GC analysis (Guérin and Abril., 2007; Kolb and Ettre, 2006; Bastviken et al., 2004):

- Use borosilicate glass bottles or vials to prevent CH₄ adsorption on the container walls.
- Clean bottles with a mild soap-and-water solution, rinse well and let dry.

⁶ Conversely, the continuous HS-GC technique or 'purge and trap' consists of retrieving continuously gas extracted from the sample phase so that equilibrium is never reached and all dissolved gases are extracted. It is applicable for volatile organic compounds (APHA-AWWA-WEF, 2005).

- Bake septum stoppers a few hours at 60°C to remove any trace of CH₄-producing chemicals.
- Base the size of bottles and the ratio of headspace to volume of sampled water (HS/S) on the gas concentration to be analysed, and on GC type and specifications. For example, when low concentrations are expected, a smaller headspace will provide better precision so a low HS/S ratio should be used. Depending on GC type, the required HS volume ranges from a few µl (for open-tubular-column GC) to 2 ml (for packed-column GC). The volume must be enough to flush the injection system (needle, syringe, connectors and tubing) and the GC internal system.
- To determine precisely the volume of HS plus S, weigh a batch of 30 bottles empty and then filled with water, and calculate the mean volume using the density of water. Repeat this every time you use a new batch, particularly if it is from a new supplier.
- Close the bottles or vials with a butyl rubber septum (higher tightness than other materials) and crimp an aluminium cap tightly over the septum using a crimping device.
- To prevent any biological activity between the time of sampling and analysis, add a preservative. Do not use acid or base preservatives (e.g., H₂SO₄ or NaOH) for CO₂ measurements as they affect pH and thus the equilibrium between the various forms of dissolved CO₂ (Figure 3.31). Salt preservatives such as KCl can be used. In that case, the solubility of gases in water is decreased so you do not need to consider gas partitioning between the two phases. HgCl₂ can be used, in which case you must consider gas partitioning between the liquid and gas phase. HgCl₂ must be handled with care because of its toxicity. Waste water from analysed samples containing HgCl₂ should be disposed of in an appropriate place.
- The HS may be created before going to the field or just before analysis. The second option reduces the risk of contamination due to leaky pierced septa but restricts the choice of preservative and ways of collecting water. The inert gas chosen to create HS will depend on budget and quality considerations. For CO₂ extraction, tests show no difference between nitrogen and argon, but argon would be more suitable for CH₄ extraction (*Lambert and*

Fréchette, 2005). Helium is more expensive but is suitable for CO₂ and CH₄ extraction. The use of glass instead of plastic syringes reduces the risk of leaks but increases the cost.

Creating HS before going to the field

- **In the lab**, use a solid preservative such as KCl (use enough to reach saturation).
- Install the septum and secure an aluminum cap with a crimping device.
- Weigh the bottles with preservative, septum and aluminum cap.
- Evacuate bottles thoroughly using a good electrical vacuum pump (note that no vacuum is perfect; a small amount of air always remains).
- Collect a certain amount of inert gas (based on the desired HS/S ratio) using a syringe and needle, and insert the needle into the septum of the sample bottle.
- **In the field**, collect water samples by inserting a needle through the septum in the water. Keep the bottle in the water until it is full (less HS).
- Note the water temperature and atmospheric pressure for the partitioning of gas between the water and gas phase during calculations.
- Place the bottles upside down to reduce leaks from the pierced septum.
- Store in a cool, dark place (e.g., in a cooler).
- Back in the lab, reweigh the bottles. The volumes of HS and S are calculated based on the difference in weight between the completely filled bottle and the bottle with HS.

Creating HS just before analysis

- **In the field**, fill bottles completely with sampled water, taking care not to produce any gas bubbles.
- Install the septum and secure an aluminium cap with a crimping device.
- Insert a liquid preservative using a syringe and needle (inserted so it is near the bottom of the bottle). Evacuate surplus water using a second needle (inserted near the surface so that the preservative is not evacuated). The amount of liquid preservative should be small enough not to affect significantly the water sample volume. KCl solution must not be used since it would significantly dilute the sampled water.

- Note the water temperature and atmospheric pressure for the partitioning of gas between the water and gas phase during calculations.
- Store in a cool, dark place (e.g., in a cooler) until processed in the lab.
- **In the lab**, weigh the filled bottles.
- Collect a certain amount of inert gas (based on the desired HS/S ratio) using a syringe (glass is better than plastic to prevent leakage) and needle, and insert the needle into the septum of the water sample, held upside down. Insert a second needle to evacuate surplus water.
- Reweigh the bottle. The volumes of HS and S are calculated based on the difference in weight between the completely filled bottle and the bottle with HS.
- Store the bottle upside down to prevent leakage from the pierced septum.

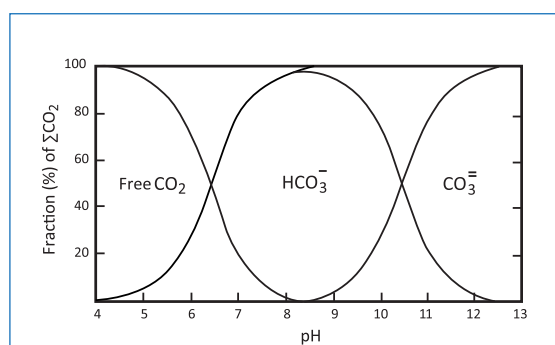


Figure 3.31: CO₂ Dissolved forms

Source: Wetzel, 2001

HS-GC analysis

HS-GC theory and practice are covered by many reference manuals (e.g., Kolb and Ettre, 2006). Specialised laboratories or universities can perform HS-GC analysis. The sample preparation steps to perform are as follows (for details, see Kampbell and Vandegrift, 1998):

- Calibrate the gas chromatographer with the gas standard.
- Let the samples reach room temperature.
- Shake the samples on a rotary shaker for five minutes.
- Inject the samples into the gas chromatographer.

A variant of the headspace method which is widely used in Brazil refers to the handling of water samples and the headspace gas: first, water is collected with a 60 ml syringe, equipped with

a 3-way stopcock. Then excess water is ejected, leaving behind the sample volume, e.g. 48 ml. The syringe is then connected to a 2l plastic bottle which had been previously filled with headspace gas, usually pure nitrogen, the bottle also being equipped with a three-way stopcock. Nitrogen is then aspirated to the syringe's 60 ml mark by moving the syringe's piston, while at the same time the plastic bottle is squeezed to ensure overpressure and exclude air. Venting the excess headspace gas from the syringe brings it to atmospheric pressure.

The syringe's stopcock is closed and the syringe is vigorously shaken for two minutes, after which the 12 ml of head space gas are transferred to a gasometric ampoule, to be taken to the laboratory for analysis.

A gasometric ampoule is a flat-bottomed glass tube equipped with a piston with a valve. Using a transfer kit, a transfer tube can be attached to the piston so that gas can be transferred into the ampoule and the valve closed.

In the laboratory, with the help of the transfer kit, the valve can be opened and gas transferred to the chromatograph's sample loop.

To fill the 2L plastic bottle with nitrogen gas to be used as headspace, the bottle is filled with water, inverted (i.e. mouth down) into a water-filled bucket and nitrogen gas, which is available at the chromatograph, is bubbled in using a 1/8 plastic tube with a copper-tube hook at its end, thus displacing the water. When full the bottle cap, equipped with the three-way stopcock, is screwed on while still under water.

Correction of HS-GC results for partitioning between the water and gas phase

Results from HS-GC analyses of water samples must be corrected for the HS/S partitioning of gases unless a salt preservative is used. Salt preservatives such as KCl decrease gas solubility and gases are thus mostly found in the HS. The difference between the gas partial pressure in water (p_{Gas}) and gas partial pressure measured by HS-GC are a function of gas solubility (K_0), gas partial pressure in the HS before equilibrium ($p_{initial}$: corresponding to the inert gas plus a certain amount of air not evacuated) and after equilibrium (p_{final} : corresponding to a mixture of gases), molar volume (V_m) and HS/S ratio:

Wind speed measurements

Wind speed can be measured on site with a portable anemometer or at a nearby meteorological station.

Correction of HS-GC results for partitioning between the water and gas phase

$$p_{Gas} = \frac{(p_{Final} * K_{0\ Equilibrium}) + ((\frac{HS}{S}) * \frac{(p_{Final} - p_{Initial})}{V_m})}{K_{0\ Sample}}$$

where $K_{0\ Sample}$ is gas solubility at the sampling temperature; $K_{0\ Equilibrium}$ is gas solubility at the equilibrium temperature, just before analysis. Partitions of CO_2 , CH_4 and N_2O are calculated using:

$$\ln K_0(CO_2) = -58.0931 + 90.5069 * (\frac{100}{T_K}) + 22.294 * \ln(\frac{T_K}{100}) +$$

$$s * (0.027766 - 0.025888 * (\frac{T_K}{100}) + 0.0050578 * (\frac{T_K}{100})^2)$$

$$\ln K_0(CH_4) = -115.6477 + \frac{155.5756}{(T_K / 100)} + 65.2553 * \ln(\frac{T_K}{100}) - 6.1698 * (\frac{T_K}{100}),$$

$$\ln K_0(N_2O) = -60.7467 + \frac{88.8280}{(T_K / 100)} + 21.2531 * \ln(\frac{T_K}{100})$$

where T_K is the temperature in degrees Kelvin, $K_0(CO_2)$ is CO_2 solubility in mole.l⁻¹.atm⁻¹ (Weiss, 1974), s is the salinity in parts per thousands, $K_0(CH_4)$ and $K_0(N_2O)$ are the CH_4 and N_2O solubility in molar fraction.atm⁻¹ (Lide, 2007). Solubility in molar fraction.atm⁻¹ is multiply by

$$(\frac{1,000 \text{ g/l [water density]}}{18.0153 \text{ g/mole [water molecular weight]}}) \text{ to obtain a solubility in mole.l}^{-1}.\text{atm}^{-1}.$$

The molar volume is calculated using:

$$V_m = \frac{nRT_K}{P} = 1 * 0.082057 * (273.15 + T) * (\frac{101.325}{P})$$

where n is the number of moles, R is the perfect gas constant (in l.atm.K⁻¹.mol⁻¹), P is the atmospheric pressure (in atmospheres), T_K is the temperature in Kelvin and T is the temperature in degrees Celsius.

WMO (2008) – No. 8, Part I – Chapter 5: Wind speed should be reported to a resolution of 0.5 m s⁻¹ or in knots (0.515 m s⁻¹) to the nearest unit, and should represent, for synoptic reports, an average over 10 min. Surface wind is usually measured by a wind vane and cup or propeller anemometer. For nearly all applications, it is necessary to measure the averages of wind speed and direction. Many applications also need gustiness data. A wind-measuring system, therefore consists of a sensor and also a processing and recording system. Simple hand-held anemometers, if they are used, should be set up and read in accordance with the maker's instructions.

Water temperature

APHA-AWWA-WEF (2005) – Standard Methods 2550: Laboratory and other non-depth temperature measurements should normally be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C. Depth temperature measurements required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate but higher cost may preclude it.

Flux calculation

Diffusive flux of gas across the thin boundary layer (TBL) can be calculated from the following equation:

$$Flux = k_x (C_{water} - C_{air}) \quad \text{MacIntyre et al., 1995}$$

where $Flux$ is expressed in mmol of CO_2 or μmol of CH_4/N_2O $m^{-2} d^{-1}$

C_{air} is the concentration of gas in the air

C_{water} is the concentration of gas in the water (obtained by the product of gas partial pressure ($pGas$) times the gas solubility (K_0) at a given temperature) obtained with:

$$C_{water} [\mu\text{mole.L}^{-1}] = K_0 [\text{mole.L}^{-1}.\text{atm}^{-1}] * pGas [\mu\text{atm}] \quad \text{Morel, 1982; Anderson, 2002}$$

$$\ln K_0(CO_2) = -58.0931 + 90.5069 * \left(\frac{100}{T_K}\right) + 22.294 * \ln\left(\frac{T_K}{100}\right) +$$

$$s * (0.027766 - 0.025888 * \left(\frac{T_K}{100}\right) + 0.0050578 * \left(\frac{T_K}{100}\right)^2) \quad \text{Weiss, 1974}$$

where $K_0(CO_2)$ is the solubility of CO_2 in water expressed in mole $l^{-1} \text{atm}^{-1}$, T_K is the temperature in Kelvin, and S is the salinity in parts per thousands. Hence, in freshwater systems, only the first part of the equation is necessary as $s = 0$.

$$\ln K_0(CH_4) = -115.6477 + \frac{155.5756}{(T_K/100)} + 65.2553 * \ln\left(\frac{T_K}{100}\right) - 6.1698 * \left(\frac{T_K}{100}\right) \quad \text{Lide, 2007}$$

$$\ln K_0(N_2O) = -60.7467 + \frac{88.8280}{(T_K/100)} + 21.2531 * \ln\left(\frac{T_K}{100}\right) \quad \text{Lide, 2007}$$

where $K_0(CH_4)$ and $K_0(N_2O)$ are the solubility of CH_4 and N_2O in mole fraction atm^{-1} and T_K is the temperature in Kelvin. Multiply by:

$$\left(\frac{1000 \text{ g/L}}{18.0153 \text{ g/mole}}\right) \quad \text{to obtain a solubility in mole } l^{-1} \text{atm}^{-1}.$$

$$\text{and with: } k_x = k_{600} \left(\frac{Sc}{600}\right)^{-x}$$

where k_x is the gas exchange coefficient expressed in cm h^{-1} , x is equal to 0.66 for wind speed $\leq 3 \text{ m s}^{-1}$ and is equal to 0.5 for wind speed $> 3 \text{ m s}^{-1}$, and Sc is the Schmidt number for CO_2 , CH_4 or N_2O which is dependent on temperature (t) in degree Celsius:

$$Sc(CO_2) = 1911.1 - 118.11t + 3.4527t^2 - 0.04132t^3 \quad \text{Wanninkhof, 1992}$$

$$Sc(CH_4) = 1897.8 - 114.28t + 3.2902t^2 - 0.039061t^3 \quad \text{Wanninkhof, 1992}$$

$$Sc(N_2O) = 2055.6 - 137.11t + 4.3173t^2 - 0.054350t^3 \quad \text{Wanninkhof, 1992}$$

and:

$$k_{600} = 2.07 + (0.215 \times U_{10}^{1.7}) \quad \text{Cole and Caraco, 1998}$$

$$k_{600} = 0.45 \times U_{10}^{1.64} \quad \text{MacIntyre et al., 1995}$$

$$k_{600} = 1.68 + (0.228 \times U_{10}^{2.2}) \quad \text{Crusius and Wanninkhof, 2003}$$

where k_{600} is the gas exchange coefficient expressed in cm h^{-1} normalised for CO_2 at 20°C in fresh water with a Schmidt number of 600. Various k_{600} equations exist in the literature and were developed for specific study sites or region.

$$\text{and: } U_{10} = 1.22 \times U_1$$

where U_1 is the wind speed at the water surface and U_{10} is the frictionless wind speed at 10 m expressed in m s^{-1} (Crusius and Wanninkhof, 2003).

The resulting final number should be multiplied by 0.24 or

$$\left(\frac{1\text{L}}{1000\text{ cm}^3} \times \frac{24\text{h}}{1\text{d}} \times \frac{10000\text{cm}^2}{\text{m}^2} \times \frac{1\text{mmole}}{1000\mu\text{mole}} \right)$$

to obtain a flux in $\text{mmole m}^{-2} \text{d}^{-1}$. Then, multiply by $44.0098 \text{ g mole}^{-1}$ to obtain a flux in $\text{mg CO}_2 \text{ m}^{-2} \text{d}^{-1}$, multiply by $16.04276 \text{ g mole}^{-1}$ to obtain a flux in $\text{mg CH}_4 \text{ m}^{-2} \text{d}^{-1}$ and multiply by $44.01288 \text{ g mole}^{-1}$ to obtain a flux in $\text{mg N}_2\text{O m}^{-2} \text{d}^{-1}$.

3.4.1.2. Bubbling – measurements using funnels

The gases generated in the reservoir sediments are initially dissolved in the interstitial water. The less soluble gases, such as CH_4 , aggregate as bubbles that can grow until the point of being liberated and migrate to the water surface. At deeper depths, bubbles dissolve in the water on their way to the water surface. Bubble fluxes mainly occur in shallow parts of reservoirs where the hydrostatic pressure is too low to dissolve CH_4 in the interstitial water. Because ebullition is not a continuous process, it is important to extend the monitoring time over days or weeks. This process can be important in regions where peatland is impounded. Ebullition is known to be an important pathway for CH_4 emissions in many peatlands (Christensen *et al.*, 2003). It can be important in warm and shallow water with high OM concentration, but it is primarily relevant in waters up to 10 m depth (Although it has been recorded at greater depths, see section 3.2.3.1.2). This implies that the bathymetry of the reservoir has to be considered when extrapolating the measurements, as shallow zones are more prone to bubbling episodes. The drawdown zone can be an important bubbling area if there is significant contribution of OM from surrounding terrestrial areas, replacing organic sediments eroded by water level fluctuation from wave action.

The occurrence of CO_2 and N_2O bubbling is rare compared to CH_4 because of the higher solubility of CO_2 and N_2O compared to CH_4 . Nevertheless, all three gases can be analyzed concomitantly with a GC.

Open floating dynamic chambers have been used to measure bubble emission (Ramos *et al.*, 2006). Ebullition and diffusive fluxes can be estimated separately using the distribution and variance in apparent piston velocities (k_{600}) from

various fluxes obtained from floating chambers (Bastviken *et al.*, 2004). Acoustic techniques have also been used to quantify bubbles (Ostrovsky, 2003; McGinnis *et al.* 2006; Ostrovsky *et al.*, 2008). The most common methods for measuring bubbling employ inverted funnels coupled to gas collectors initially filled with water, which capture the ascending bubbles. Bubble collectors installed below wind-wave influence can be used to integrate bubble emission over time and are cheap and easy to operate.

Samples are collected using a set of funnel collectors. If the environment is believed to emit small amounts of bubbles, large bubble collectors should be installed for longer periods of time to maximize potential bubble collection. In most cases, the funnels are placed along transects from the shallows to the deepest regions. The funnels are submersed and all air is removed to avoid contamination by atmospheric air. The collecting bottles, full of water, are then coupled to the funnels. The choice of sampling site and the arrangement of funnels are determined by variables such as the density of flooded vegetation, number of years since impoundment, depth, presence of semi submerged vegetation, soil/sediment composition and geographic region of the reservoir. The water flow should be near zero and the bottom slope should be less than 20 deg. for the system to remain stable over a long period.

3.4.1.2.1. Funnel design

Below is the list of materials required to build funnels. This list is given as an example; other designs may be used. However, it is important to realise that the material chosen for the funnel and gas-collection bottle will affect the sampling interval. The sampling interval must not exceed 24 hours to avoid diffusion of CH_4 through plastic material and redissolution of CH_4 in water.

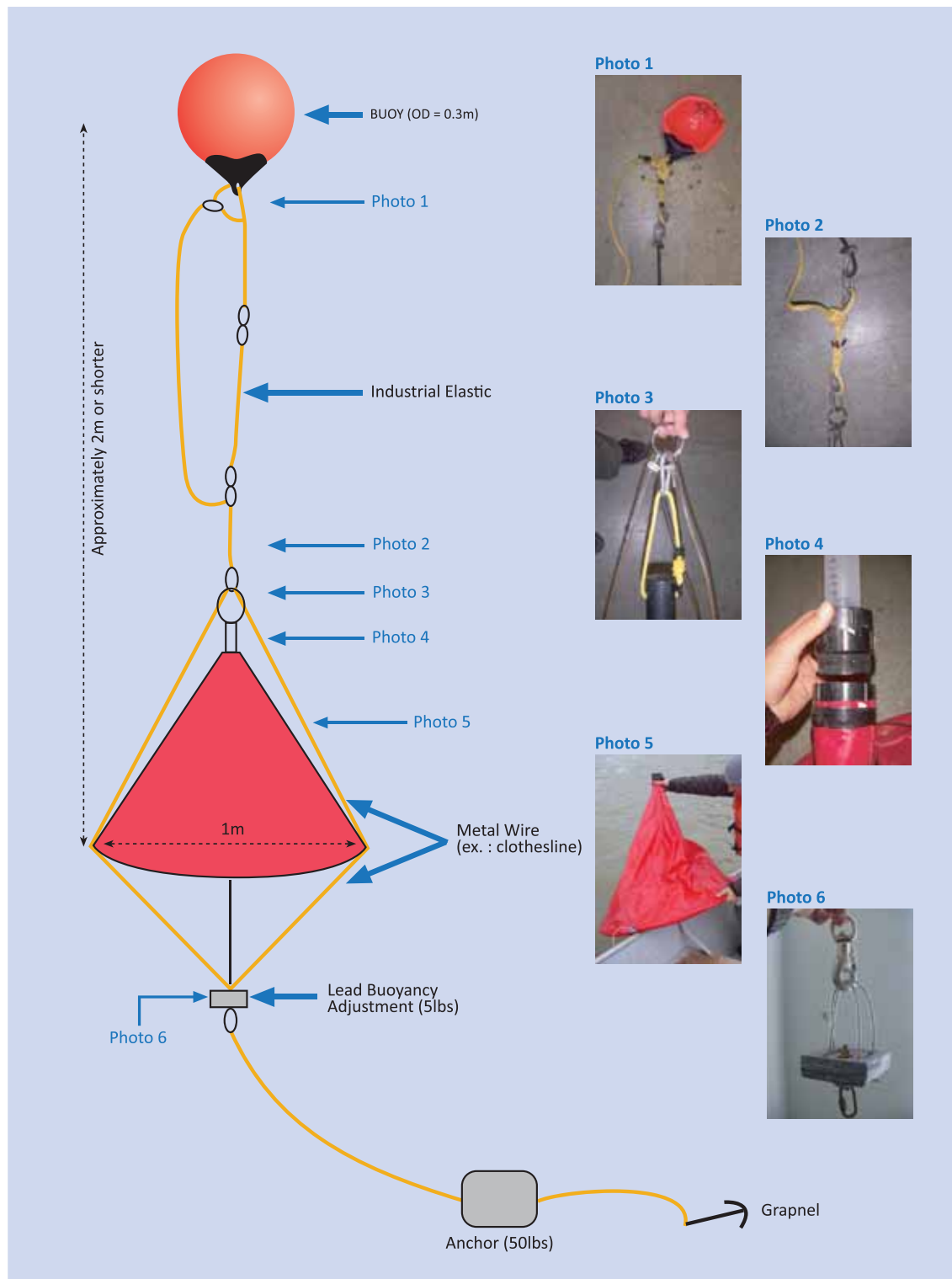


Figure 3.32: Schematic representation of a gas-collecting funnel

Example of materials required to build funnels for windy conditions (large waves):

- 1 aluminium ring, 1 m diameter
- PVC canvas
- Collecting bottle
- 6 steel wires (clothes line), 1.2 m
- 2 steel rings, 40 mm
- 12 cable screws
- 1 lead weight, 2.5 kg
- 2 eye bolts, 50 mm
- 4 repair links
- 1 plumbing collar



Figure 3.33: Stack of funnels (with zippered-in hoops, tied together to form a string and with buoys attached) ready to be taken to deployment site

- 1 swivel
- ABS tubing and fittings, 50 mm
- syringe with 2-way valve, 150 ml
- 1 toilet check valve
- 1 bungee cord, 1 m
- 1 buoy, 300 mm diameter
- 1 anchor
- Rope.

The PVC canvas is sewed into a funnel shape and fixed onto the aluminium ring. The ABS tubing and fittings are tied to the small end of the funnel using the collar. The syringe fits perfectly into the tube thread and the check valve is used as a gasket. The fittings are arranged so that the syringe is always protected and easy to install or retrieve. The funnel is installed mouth down and is held in place by six steel wires. The top wires are tied to the buoy with a bungee cord and secured with a rope. A lead weight is attached to the end

of the bottom wires to keep the funnel upright in the water. A swivel is installed between the lead weight and the anchor line to prevent the system twisting. This design absorbs the effect of waves on the buoy, but requires water at least 3 m deep because of its length (Figure 3.32).

Another example is a foldable funnel (umbrella-type), designed to be stowed in a suitcase as a set of 15 (Figure 3.33). These funnels are intended to be deployed in transect strings e.g. with two funnels at 5 m depth, two at 10 m and one at 20 m.

A simpler system, for areas where very high bubbling is expected or with little or no wind and wave action, consists of a simple funnel with a septum at the narrow end. The gas is thus stored inside the funnel rather than in a syringe (small volume). This design is shorter and can be installed in shallower, calm areas (no wind and waves). The angle of the funnel may be adjusted in either design, depending on water turbulence and waves. Larger angles can be used in calm waters.

3.4.1.2.2. Collecting gas from funnels

The monitoring period may last from several days to weeks or the whole season. Visit the funnels regularly (daily) to ensure gas is collected and to avoid redissolution in water. If you use a syringe to collect gas, note the volume of gas collected before introducing gas into subsample vials or gasometers. If you use a funnel with a septum, retrieve all the gas and note the total volume. The collection bottles must be hermetically sealed while still under water and are collected for later laboratory analysis. One potential problem with

long periods between sample collections from funnels is underestimated fluxes due to microbial oxidation of the trapped methane.

If a portable GC analyser is used, gas samples can be collected with plastic syringes and analysed the same day. If you expect to conduct analyses more than 12 hours after collection, you should collect gas samples in evacuated borosilicate vials or with a gasometer. Borosilicate vials are much cheaper to use but contamination may occur during handling due to needles and through perforated septa. One way to reduce contamination is to introduce a small quantity of saturated saltwater in the evacuated vial and store the vial upside down.

3.4.1.2.3. Calculating bubbling fluxes

Gas concentration, sampling interval and funnel area are needed to compute bubbling fluxes. Gas concentration in ppm measured with GC can be converted into concentration in mg m^{-3} using the perfect gas formula (for air concentration only). If the sampling interval is 12 hours or less, atmospheric pressure ($AtmP$) and water temperature (T) can be used in the concentration conversion calculation. For longer sampling intervals, you can use mean water temperature and atmospheric pressure. If the concentration of bubble gas is obtained by chromatographic analysis of gas samples, then (assuming the gas sample is in equilibrium with atmospheric pressure and the temperature of the laboratory) use atmospheric pressure and the temperature of the laboratory. If the atmospheric pressure was not recorded, a standard atmospheric pressure of 101.325 kPa can be used.

Calculating bubbling fluxes

$$GasConc.[\text{mg.m}^{-3}] = \frac{GasConc.[\text{ppm}] * MolecularWeight[\text{g.mole}^{-1}] * AtmP[\text{KPa}]}{8.3144\text{J.K}^{-1}.\text{mole}^{-1} * (273.15\text{K} + T[^\circ\text{C}])}$$

Bubbling fluxes can be calculated using:

$$BubblingFluxes[\text{mg.m}^{-2}.\text{d}^{-1}] = \frac{GasConc.[\text{mg.m}^{-3}] * GasVol.Collectd[\text{m}^3]}{FunnelArea[\text{m}^2] * SamplingInterval[\text{days}]}$$

The emission value calculated by this formula gives the emission at one point. The bubble-emitting regions are the shallower parts of a water body, reaching from the shore to a depth of 20 to 30 m. To report bubble emission flux of a gas, two values should be cited: the average emission in the bubble-emitting zone and its average over the whole water surface. To find the area of the bubble-emitting zone, use the averages of measured emission intensities at, say, 5 m, 10 m and 20 m depths. From the straight line fitted to the emission vs depth data, it is possible to find the depth H beyond which bubbling ceases. The bubble-emission zone is the band along the shore going from zero depth to depth H.

3.4.1.3. Downstream emissions

Downstream emissions are those observed below reservoir outlets (turbines, spillways, low-level outlets, etc.). They are composed of degassing and diffusive fluxes, and their influence may range from a few tens of metres up to 50 km downstream in the river (Abril *et al.*, 2005).

3.4.1.3.1. Degassing

Degassing is defined in section 2.4.1.2.3 as an emission which happens on discharge from low-level outlets, including turbine tailwater (induced by dramatic pressure change). Degassing downstream of a dam and spillway can be estimated by the difference between the gas concentration upstream (or in the turbine) and downstream of the power plant multiplied by the outlet discharge (see below for calculation). CH₄ is more susceptible to be degassed compared to CO₂ and N₂O because of its lower solubility. However, all three gases should be monitored for degassing.

Determining upstream concentration at or near the water intake

To accurately determine degassing, take samples of water entering the turbines directly at the turbines or at the powerhouse intake. If possible, sample the gas concentrations from ports in the conduits leading to the outlets. If that is not feasible, degassing may be evaluated from the average GHG concentration across vertical profiles in the reservoir (with or without stratification) since the water intake creates a conic turbulence in front of it. Determining the stratification is also useful for data interpretation.

Water profiling of temperature, oxygen and dissolved gas should be performed upstream of the

dam to determine whether there is stratification of the water column near the intake. Temperature and oxygen profiles are easy and cheap to measure and help detect any stratification. Once those profiles are measured, gas partial pressure profiles can be obtained using in situ sensors or by collecting water samples at various depths. If water samples are collected, CH₄, CO₂ and N₂O concentrations can be determined by the headspace method followed by gas chromatography analysis (see section 3.4.1.1.3 – Gas partial pressure measurements – Headspace gas chromatography).

Determining downstream concentration

The concentration in water after it passes through the turbine and spillway can be determined in water samples taken outside the area of turbulence downstream of the dam (around 500 m from the dam). Water sample GHG concentrations can be determined by the headspace method followed by gas chromatography analysis (see section 3.4.1.1.3 – Gas partial pressure measurements – Headspace gas chromatography).

If downstream concentration cannot be measured, it can be assumed that downstream concentrations are in equilibrium with the atmosphere. This method requires less monitoring effort but has the disadvantages of overestimating the overall degassing fluxes and altering the true ratio of CO₂ and CH₄ degassing.

Determining water discharge

WMO (1994) – No. 168, Chapter 11: River discharge, which is expressed as volume per unit time, is the rate at which water flows through a cross-section. Discharge at a given time can be measured by several methods, and the choice depends on the conditions at a particular site. A number of approaches are outlined below.

- Measurement of discharge by current meters: general steps include selection of sites, measurement of cross-sections, measurement of velocity, and computation of discharge.
- Measurement of discharge by the float method: general steps include selection of sections, selection and installation of floats, measuring procedure, computation of velocity, and computation of discharge.
- Measurement of discharge by dilution methods: general steps include selection of site, use of tracers and detection equipment, and computation of discharge.

- Measurement of corresponding stage: stage and corresponding time are noted at intervals to identify segments of total discharge with time and stage.
- Computations of discharge by indirect methods: the peak discharge may be determined after the flood has subsided by computations that combine well-established hydraulic principles with field observations of channel conditions and flood profiles. All the methods involve the simultaneous solution of continuity-of-mass and energy equations. Such computations may be made for reaches of a river channel, through roadway culverts and bridge openings, and over dams and highway embankments. Although the hydraulic formulae differ for each type of waterway, all the methods involve the following factors:
 - geometry and physical characteristics of the channel and boundary conditions of the reach used;
 - water surface elevations at the time of peak stage to define the cross-sectional areas and the head difference between two significant points;
 - hydraulic factors, such as roughness coefficients based on physical characteristics.
- Measurement of discharge under difficult conditions: such conditions include unstable channels, mountain streams, or measurement of unsteady flow.
- Other methods of stream gauging: moving-boat method, ultrasonic (acoustic) method, electromagnetic method.

3.4.1.3.2. Fluxes in the downstream aquatic system

Downstream diffusive fluxes are defined in section 2.4.1.2.3. Diffusive and bubbling fluxes should be measured in the aquatic system downstream of the (proposed or existing) dam up to a maximum distance of 50 km. This distance may vary from site to site and must be assessed for each project. Comparing emissions in the aquatic system downstream of the dam before and after impoundment will indicate whether leakage from the reservoir is affecting the downstream ecosystem. The methods in sections 3.4.1.1 and 3.4.1.2 can be used.

3.4.2. Carbon and nitrogen stock

Carbon and nitrogen content in water should be measured at representative stages in stream hydrographs and, when combined with discharge calculations, allow carbon transport to be determined. Carbon and nitrogen stock in the water column and in sediment should be determined as described below.

3.4.2.1. Carbon and nitrogen availability in water column/transport

Carbon present in the water column is subject to transport downstream from the reservoir. The evaluation of the carbon stock present in the area to be flooded by the reservoir is a critical measurement, as it can be used as an indicator of future reservoir GHG emissions, GHG emissions being proportional to the content in organic matter flooded (see section 2.2.2.1).

Most lakes are supersaturated in CO₂ (*Del Giorgio et al., 1999*), and thus generally emit CO₂ to

Calculating degassing

The degassing flux ($Flux_{Degassing}$) is calculated as follow:

$$Flux_{Degassing} = ([Gas]_{UpT} - [Gas]_{downsT}) \times Q_T + ([Gas]_{UpS} - [Gas]_{downsS}) \times Q_S$$

where $[Gas]_{UpT}$ is the gas (CH₄, CO₂ or N₂O) concentration upstream of the generating station (turbines) expressed in mg/m³ (obtained using the solubility equations – see section 4.1.1.3), $[Gas]_{downsT}$ is the gas concentration downstream of the generating station, Q_T is the turbine flow and $[Gas]_{UpS}$, $[Gas]_{downsS}$, and Q_S are equivalent terms for the spillway.

The flow should be for the same time period as gas concentration measurements. The best-case scenario would entail continuous gas concentration measurements (e.g., every three hours), averaging concentrations for each day and calculating using the mean daily flow (turbine and spillway). If the operating mode (peaking) is expected to vary on an hourly basis, it may then be useful to calculate de-gassing fluxes for every hour. The gas concentration sampling interval should thus be determined on the basis of the operating mode.

the atmosphere. CO₂ saturation is linked to the dissolved organic carbon (DOC) concentration (Prairie *et al.*, 2002). DOC is degraded by various processes including biological degradation and photo-oxidation into dissolved inorganic carbon (DIC).

Organic matter comprises particulate and dissolved organic carbon (POC, DOC) and organic compounds containing sulphur (S), nitrogen (N) and phosphorus (P). Carbon (C) in a water body can be in particulate or dissolved form, and can be organic and inorganic. Below is a description of the processes producing DOM, TOC, DOC, TIC and DIC.

3.4.2.1.1. Dissolved organic matter (DOM)

DOM can be of autochthonous or allochthonous origin. Autochthonous DOM in aquatic ecosystems is produced by photosynthesis (Häder, 1997), extracellular release and exudation mechanisms, or by the degradation of plankton and macrophytes (e.g., mortality, grazing, biodegradation, photodegradation) (Obernosterer *et al.*, 1999). Allochthonous DOM, by contrast, originates from terrestrial input from the catchment (Hessen, 2002). The proportion of allochthonous and autochthonous DOM is influenced by the degree of aquatic productivity, precipitation, terrestrial inputs and elevation (Williamson *et al.*, 1996).

The majority (> 50%) of freshwater DOM (Corin *et al.*, 1996; Ertel, 1990; Wetzel *et al.*, 1995; Davies-Colley and Vant, 1987; Reche *et al.*, 1999; Moran and Hodson, 1990) comprises dissolved humic substances (DHS). Dissolved humic substances are dark coloured, acidic and composed mainly of aromatic molecules (Gastonguay *et al.*, 1995) from terrestrial plant material.

3.4.2.1.2. Total organic carbon (TOC)

TOC is the quantity of carbon present in the organic matter, i.e., all carbon atoms covalently bonded in organic molecules. TOC can be in the dissolved form (DOC – the fraction of TOC that passes through a 0.45 µm pore-diameter filter) and in suspended or particulate form (POC – also referred to as non-dissolved organic carbon, the fraction of TOC retained by a 0.45 µm pore-diameter filter) (APHA-AWWA-WEF, 2005).

3.4.2.1.3. Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) is the fraction of TOC that passes through a 0.45 µm pore-diameter filter (APHA-AWWA-WEF, 2005). Decomposition of DOC is often one order of magnitude greater than

that of POC and is also accelerated by photolysis and its subsequent bioavailability, contributing to the efflux of CO₂ to the atmosphere (Wetzel *et al.*, 1995).

3.4.2.1.4. Dissolved inorganic carbon (DIC)

DIC is also referred to as total inorganic carbon (TIC). DIC represents the total of the three CO₂ aqueous forms: HCO₃⁻, CO₃²⁻ and free CO₂. The equilibrium between these three CO₂ forms depends on pH. DOC is transformed into DIC by photo-oxidation (Ertel, 1990; Petterson *et al.*, 1997; Dahlen *et al.*, 1996; Vodacek *et al.*, 1997) and micro-organism respiration (Cole, 1999).

The type of DOM and the DIC concentrations are sometimes linked. In eutrophic lakes with high primary production (high chlorophyll concentrations and high concentration of autochthonous DOM) the CO₂ uptake by photosynthesis is high relative to the respiration and mineralization processes. Such lakes therefore typically emit less CO₂ to the atmosphere than humic oligotrophic lakes where mineralization processes producing CO₂ dominate over primary production (Bertilsson and Tranvik, 2000).

The DIC production at the sediment-water interface is influenced mainly by the amount and quality of the sediment organic matter.

3.4.2.1.5. Ammonium, nitrites and nitrates

Ammonium (NH₄⁺), nitrites (NO₂⁻) and nitrates (NO₃⁻) are the three soluble forms of nitrogen susceptible to being transformed into N₂O. In aerobic waters, N₂O is a by-product of the nitrification of NH₄⁺. In anaerobic waters, N₂O is a by-product of the denitrification of NO₂⁻ and NO₃⁻. Below are the methods used to determine NH₄⁺, NO₂⁻ and NO₃⁻.

Ammonia nitrogen

APHA-AWWA-WEF (2005) – Standard Method 4500-NH₃: this method applies to measurements in drinking and surface waters, and in domestic and industrial wastes. Dissolved ammonia (NH₃(aq) and NH₄⁺) is converted to NH₃(aq) by raising pH. NH₃(aq) diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode.

USEPA (1993) – Method 350.1 Revision 2: this method covers the determination of ammonia in drinking, ground, surface and saline water, and in domestic and industrial wastes. The sample

is buffered and distilled into a solution of boric acid. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue, which is proportional to the ammonia concentration. The blue colour formed is intensified with sodium nitroprusside and measured colorimetrically.

ASTM (2008) – Standard Test D1426-08: this is an ion-selective electrode method. It is applicable to the determination of ammonia nitrogen in reagent and effluent water. The test method is applicable to surface and industrial water, and to wastewater after distillation.

Total Kjeldahl nitrogen

APHA-AWWA-WEF (2005) – Standard Method 4500-N org. B: this is acid digestion, distillation and determination with a specific electrode.

In the presence of H_2SO_4 , potassium sulfate (K_2SO_4) and a cupric sulfate ($CuSO_4$) catalyst, the amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After addition of a base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined colorimetrically, by an ammonia-selective electrode technique, or by titration with a standard mineral acid.

ASTM (2006) – Standard Test D3590-02: the standard contains the manual digestion/distillation method and the semi automated colorimetric Bertholt method.

Nitrites and nitrates

APHA-AWWA-WEF (2005) – Standard Method 4500- NO_3^- : NO_3^- is reduced almost quantitatively to nitrite (NO_2^-). The NO_2^- thus produced is determined by the formation of a highly coloured azo dye that is measured colorimetrically.

ASTM (2009) – Standard Test D3867-09: these two test methods cover the determination of nitrite

nitrogen, nitrate nitrogen, and combined nitrite-nitrate nitrogen in water and wastewater. They are test method A – automated cadmium reduction; and test method B – manual cadmium reduction. These methods are applicable to surface, saline, waste and ground water.

USEPA (1993) – Method 353.2 Revision 2.0: this method covers the determination of nitrite alone, or nitrite and nitrate combined in drinking, ground and surface water, and in domestic and industrial wastes. A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite is treated to form a highly coloured azo dye, which is measured colorimetrically.

3.4.2.1.6. C:N:P ratio

Elemental chemical composition of planktonic particulate organic matter reflects the planktonic structure as well as biochemical processes (Table 3.7). Phosphorus (P), and to a lesser extent nitrogen (N), are limiting elements for freshwater plant productivity. Limitation in these elements can lead to alteration in cell content and to the C:N ratio. The carbon content of organic matter is on average at least an order of magnitude greater than that of nitrogen (N). The C:N ratio for allochthonous DOM varies from 45:1 to 50:1, and for autochthonous DOM it is 12:1 (Wetzel, 2001). The majority of N is proteinaceous in the plankton.

Determination of the trophic state (autotroph vs. heterotroph) of a water body can be based on its content in total nitrogen (TN) and total phosphorus (TP; Figure 3.34). Primary productivity, phytoplankton density and biomass, chlorophyll a, dominant phytoplankton, light extinction coefficient, TOC and total inorganic solids are other characteristics of trophic status (Wetzel, 2001).

Table 3.7: Type of organic matter and C:N:P ratio

Type of organic matter	C:N:P ratio
Allochthonous DOM	C:N varies from 45:1 to 50:1
Autochthonous DOM	C:N ~ 12:1
Streams, shallow lakes, reservoirs with short residence times	C:P<350 N:P<26
Streams, shallow lakes, reservoirs with short residence times > 6 months	C:P>400 N:P>30
Tropical lakes	High C:N

Source: Wetzel, 2001

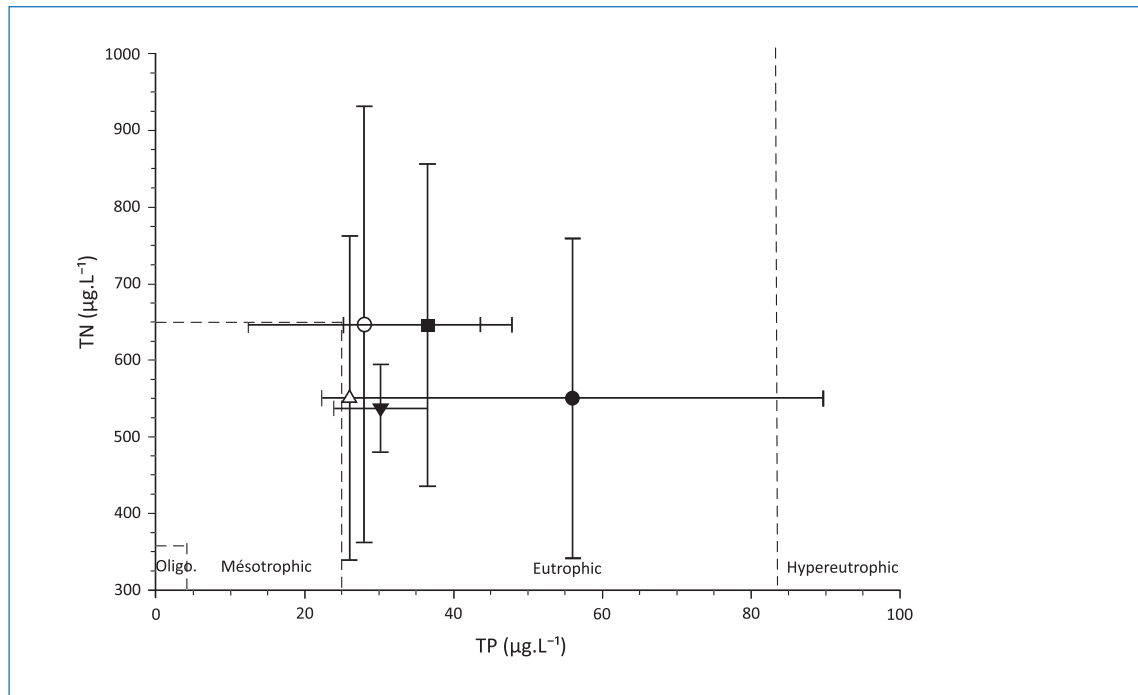


Figure 3.34: Trophic state determination based on TN and TP

Data are shown as an example.

Graph based on Wetzel's (2001) relationship of lake productivity to N and P concentrations.

3.4.2.1.7. Origin of organic matter – $\delta^{13}\text{C}$ analysis

The origin of organic matter can be assessed by $\delta^{13}\text{C}$ analysis (Hélie, 2004). There are three isotopes of carbon: ^{12}C , ^{13}C and ^{14}C (in order of importance). Plants use two types of atmospheric carbon during photosynthesis: ^{12}C and ^{13}C . Various $^{12}\text{C}:^{13}\text{C}$ ratios are found in plants depending on plant types (C3 vs. C4: mainly grass and sedge families). If terrestrial plants use air CO_2 , which has a mean $\delta^{13}\text{C}$ value of -8‰, aquatic plants use dissolved CO_2 , which has more variable $\delta^{13}\text{C}$. The use of $\delta^{13}\text{C}$ -OM signatures to identify aquatic against terrestrial production is largely site specific. However, in some cases it provides a relatively sensitive indicator of their ratio in riverine OM fluxes (Rau, 1978; Barth, 1998).

3.4.2.1.8. Collection of samples in the water column

To estimate the carbon stock in the water column, water samples must be collected from various depth increments using a water sampler (Figure 3.35). Types of samples include (WMO, 1994):

- **Grab samples.** These are used to characterise water quality at a particular time, location and depth. Grab samplers may be categorised into those appropriate for non-volatile constituents and those suitable for dissolved gases. Van Dorn bottles, Kemmerer samplers and (diaphragm, peristaltic or rotary) pumps may be used for DOC sampling.

- **Composite samples.** These are obtained by mixing several discrete samples of equal volume. Composite samples provide average water quality conditions over the time of sampling. It is more economical since fewer samples are needed. There are two types of composite samples: sequential (i.e., at a regular time interval) and flow-proportional.

Collection of representative samples will depend on site characteristics: depth-integrated water samples are suitable for a uniform, well-mixed water column, whereas samples at various depths and distances along the cross-section of a river may be needed in other cases (WMO, 1994). DOC content should be assessed for the entire volume of the river or reservoir, so the sampling plan must be developed accordingly, considering (vertical and horizontal) spatial variability.

For some analyses like DOC determination, filtration is necessary to separate particulate from dissolved matter. The time between sample collection, filtration and analysis in the laboratory must be minimized or a preservative technique used (or both). The preservative technique will depend on the analysis, but in general the following rules apply:

- Keep samples in a cool (4°C or on ice), dark place, such as a cooler.
- Add a chemical preservative if needed. These are often provided by the laboratory that is to

Carbon entering the reservoir can be estimated as follows:

$$C_{Stock} = (DOC_{Inlet} \times Q_{Inlet}) + (DOC_{Soil} \times Q_{Soil}) + (DOC_R \times Q_R)$$

where C_{Stock} is the carbon stock of the reservoir/river, DOC concentration and water flow (Q) are measured at each inlet of the reservoir/river, in drainage basin soils (see Section 3.2.2.4), and in the reservoir/river itself. DOC should be assessed for the whole volume of the reservoir/river.

Carbon leaving the reservoir ($C_{Leakage}$) can be estimated as follows:

$$C_{Leakage} = DOC_{Dam} \times Q_{TS}$$

where DOC is measured in the water column in front of the dam and Q_{TS} is the sum of the turbine and spillway flows.

other biochemicals contained in the tissues of living benthic micro-organisms, and the detritus of organisms formerly living in the lake and its catchment (Meyers and Ishiwatari, 1993).

Bacterial activity, carbon oxidation (degradation process), bioturbation and resuspension of sediment that occur at the water/sediment interface (active layer) affect the carbon storage estimation in sediment surface layers (Meyers and Ishiwatari, 1993).

Once buried below the zone of bioturbation, organic matter is subject to further bacterial degradation, often resulting in methanogenesis. Only less reactive forms of organic matter accumulate in the sediments. Under that 'active zone,' most of the sediment carbon is permanently buried and not involved in the biogeochemical processes (Sobek et al., 2006).

Carbon in sediment is mainly found in the form of particulate organic carbon (POC). The International Organization for Standardization (ISO) provides guidance on sampling bottom sediments (Appendix 3.1 – International Organization for Standardization, Guidance and Sampling Procedures, ISO 5667-12:1995). Sediment samples can also be collected as described in Environment Canada (2002 a and b). The choice of sampling method must consider hoisting equipment available; physical constraints of the environment (e.g., bathymetry, currents and waves); the penetration depth required; sample integrity; the type of material used to make the sampler (plastic should not be used for organic analyses); and the sample volume required (Environment Canada, 2002 a and b; Figure 3.36).

- Sediments

- Grab samplers. Samplers equipped with a set of jaws and suitable for high-volume sampling of homogenous sediment. Grab sampler types include Ekman, Ponar, Van Veen, Shipek, Smith-McIntyre and US BM54 samplers.
- Corers. Tubes sunk into the sediment by various means to obtain a core of known length. Corers usually make it possible to characterise the entire depth of sediment and to get unmixed sediment samples. Corer types include:
 - hand/mechanical corers – deployed by a diver or a rod (piston);
 - gravity corers – open-barrel or piston-/cable-operated;
 - vibratory corers.

Subsampling of cores or grab sampling must be carried out for subsequent laboratory analysis.

Pore water fills the interstices between sediment particles. In general, concentrations of different substances tend to reach an equilibrium between pore water and sediment (Environment Canada, 2002 b). Pore water can be used to assess the mobility of carbon from the sediment into the water column. However, pore water extraction methods usually affect DOC content.

- Direct methods

- dialysis (may be used to extract dissolved gas)
- direct suction.

- Indirect methods

- centrifuging
- squeezing.

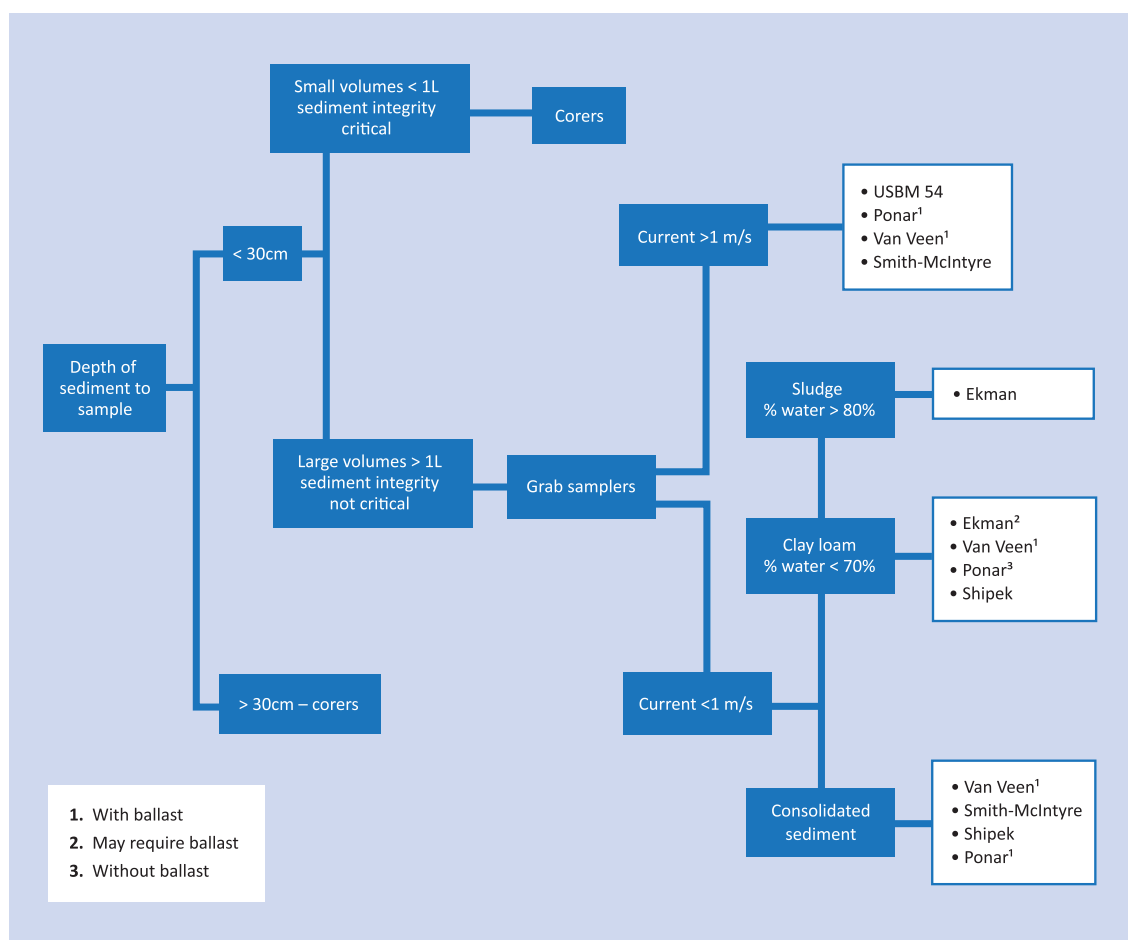


Figure 3.36: Selection of sediment sampler

Detailed sampling methods, sample acceptability criteria, sample manipulation and conservation methods are described in Sediment Sampling Guide for Dredging and Marine Engineering Projects in the St. Lawrence River, Volume 2, Field Operations Manual (see Appendix 3.1). Further information can be found in Bisutti *et al.* (2004) and in Mudroch and MacKnight (1994).

3.4.2.3. Determining total, organic and inorganic carbon (TC, TOC and TIC)

Carbon analysis (TC, TOC and TIC) from sediment or water samples (or soils for the terrestrial ecosystem; see sections 3.2.2.2 and 3.2.2.4) can be analysed with an elemental automated carbon analyser. The main steps in determining carbon in water are described in APHA-AWWA-WEF (2005) – Standard Methods 5310, and can be summarized as follows:

1. Filtration separates the particulate from the dissolved form of carbon using filters with a pore size of 0.45 µm. Use an electrical or manual pump to create the vacuum in the filter apparatus. Analyse the filtrate for DOC concentration and the filter for POC. Send water samples (filtrate) and filters to a

specialised laboratory for analysis or analyse them in a field lab at the end of the day using an elemental automated carbon analyser (steps 3-6).

2. Inorganic carbon is removed by acidification and sparging.
3. The remaining carbon (assumed to be of organic form) can be oxidised by the Combustion-Infrared method, the Persulfate-Ultraviolet oxidation method, the Wet-Oxidation method (APHA-AWWA-WEF, 2005), or with ozone or UV fluorescence (Kolka *et al.*, 2008). For determination of carbon in soil, dry combustion at high temperature is the recommended method as wet combustion can lead to underestimation of carbon content (Burton and Pregitzer, 2008).
4. Measure the CO₂ generated by the oxidation process (Kolka *et al.*, 2008). The amount of CO₂ generated at this step corresponds to the TOC concentration.
5. Record the total carbon (TC) generated at steps 2 (inorganic – TIC) and 4 (organic – TOC).

6. TIC concentration is the difference between TC and TOC.

QA/QC items:

- Many kinds of filters may be used but it is important that they do not release any DOC during filtration (*Kolka et al., 2008*). During or immediately after collecting samples, use a glass-fibre filter (to reduce adsorption of DOC on the filter) or metal membrane to filter for DOC (*WMO, 1994*).
- Wash the filter and filter apparatus with the sample water by discarding the first 200 ml of filtrate.
- All traces of acid must be removed from the samples by complete drying to avoid interference with the analyser's infrared detector.

3.4.2.4. Sediment sampling for gas analysis

Since the major source of carbon gases in reservoirs is the bottom deposits, carbon budgets must include their sediment gases. Carbon budgets must include all pathways. Fluxes of carbon gases to and from the sediments represent important links with other ecosystem processes.

Sediment samples for gas analysis have been routinely collected by gravity coring. If the cores are lowered slowly into the bottom sediments so as not to disturb and disrupt bubbles, gas concentrations including CH₄ in gravity core-collected sediments compared favourably with other sampling techniques, such as coring with the aid of scuba divers (*Adams and Baudo, 2001*) and subsampling of box cores (*Adams 1991*).

Sediment core processing for gas analysis is usually carried out with a core adaptor sampling system (*CASS; Adams, 1994*) or with a slicing system developed for 5mm sediment core sectioning for gases called the A-N sediment gas sampler, UWITEC, Mondsee, Austria (*Abe et al. 2005*). In both cases, sediment core is carefully sliced and extruded into a gas-tight syringe and gas concentrations are measured by gas chromatography with the headspace technique.

The gas concentration of the overlying water above the sediment-water interface and at the near-surface sediment layer are measured. Then the diffuse fluxes of pore water gases to the sediment-water interface are calculated using Fick's first law of diffusion according to *Adams (2005)*.

3.5. Gas analysers and gas measurement technologies

3.5.1. Gas chromatography (GC) analysis

Gas chromatography can be used to analyse dissolved gas in water using the headspace technique as briefly described in section 3.4.1.1.3 or simply for analysing gas in air samples such as those collected from the soil/low vegetation chamber method (section 3.3.1.2.1) or from the aquatic diffusive surface flux chamber method (section 3.4.1.1.1). CH₄ is analysed with a GC equipped with a flame ionisation detector (GC-FID), CO₂ with a thermal conductivity detector (GC-TCD), and N₂O with an electron capture detector (GC-ECD). General gas chromatography principles and techniques are described in handbooks such as those by McNair and Miller (2009) and Willard et al. (1988).

3.5.2. Infrared gas analysers (IRGAs)

All such analysers have two main components: a light source and a detector. Open-path analysers have an open path between the detector and light source, whereas in closed-path systems the light source and detector are enclosed in a sample chamber or light tube.

Key features for good measurements are pressure and temperature compensation (*Hashmonay and Crosson, 2009*). Some instruments measure pressure and temperature, and automatically compensate for variations in those variables, while others do not.

The gas analysers or technologies listed below can be used for measurements in both terrestrial and aquatic systems. Appendix 3.2 lists a number of suppliers and cost estimates. Figures 3.5 and 3.6 presents advantages and constraints of the various technologies. Analyser techniques depend on light source type (mid- to near-infrared) and how the light spectrum is treated (position of filter, mirror types and numbers).

- Non-dispersive infrared (NDIR): the term 'non-dispersive' refers to the fact that all the light passes through the gas sample and is filtered just before the detector.
- Fourier-transformed infrared (FTIR): measurements of electromagnetic or other types of radiation.
- Tunable diode laser spectroscopy (TDLS): uses a tunable (adjustable) diode laser source

that emits in the mid-infrared spectral region (between 3 and 30 μm).

- Cavity ring down spectroscopy (CRDS): a typical CRDS setup consists of a laser that is used to illuminate an optical cavity, which in its simplest form consists of two highly reflective mirrors.

NDIR instrument is suitable for CO_2 and CO detection (but not CH_4 and N_2O), while FTIR is suitable for CH_4 , CO_2 and N_2O detection. According to Tremblay et al. (2005), the accuracy of the instrument in the 350-500 ppm range is of 0.2 to 0.5 ppm for the NDIR and 1% of the range with the FTIR, 3 to 5 ppm for the CO_2 .

3.5.3. Automated systems

Automated systems combine a measuring instrument with a programmed data logger to sample at fixed intervals. Continuous measurements may clearly reveal seasonal trends in GHG and ancillary variables. This type of system should be used to the extent possible for both terrestrial and aquatic GHG variable monitoring.

For example, in aquatic ecosystems, continuous measurement of gas partial pressure highlights the importance of seasonal and annual variations (Figure 3.37) on GHG emissions. In boreal reservoirs, the use of automated systems has clearly shown: 1) a significant increase of pCO_2 under the ice cover; 2) a decrease in pCO_2 in spring corresponding to the ice-melting period; and 3) lowest pCO_2 in late spring or summer, depending on the ecosystem (Demarty et al., 2009).

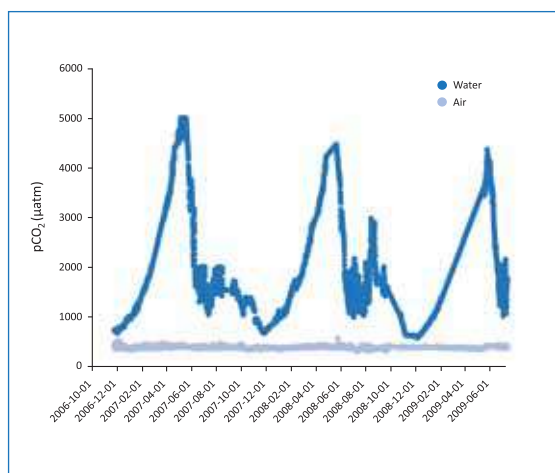


Figure 3.37: pCO_2 data collected using a CO_2 analyser and a datalogger at Eastmain-1 reservoir

Source: Hydro-Québec and Environnement Illimité Inc.

3.6. Ancillary measurements

Certain ancillary variables are not necessary for any GHG measurements and calculations, yet represent precious information for a comprehensive understanding of the trends in GHG emissions. Some of these variables are listed below. Various standard measurement protocols exist from national and international agencies. The International Organization for Standardization (ISO) provides protocols for many of the variables presented below and elsewhere in the manual such as pH, conductivity and TOC (Appendix 3.1). Other equally good standards may exist elsewhere. Table 3.8 presents a summary of ancillary variables and their role.

3.6.1. Water quality

For water quality variables, samples should be collected with a water sampler-integrator (Figure 3.35) of the photic zone (1 to 10 m). If the depth exceeds 10 m, a bottom sample should also be collected.

3.6.1.1. Dissolved oxygen

Dissolved oxygen (DO) is used as an indicator of the metabolism of a water body. High DO correlates with systems having high primary productivity (also called 'autotrophic systems'), whereas low DO correlates with a high respiration rate and thus systems having high secondary productivity (also called 'heterotrophic systems'). DO profiles reveal the potential for methane storage in the water column since high CH_4 concentrations require anoxic conditions.

WMO (1994) – No. 168, Chapter 17: the WMO suggests that the dissolved-oxygen concentrations may be determined directly with a DO meter or by a chemical method, such as Winkler analysis.

APHA-AWWA-WEF (2005) – Standard Method 4500-O: the Winkler, or iodometric method, consists of oxidation of DO by addition of divalent manganese solution, followed by a strong alkali. The iodine obtained is then titrated with a standard solution of thiosulfate. The titration end point can be detected visually, with a starch indicator, or electrometrically, with potentiometric or dead-stop techniques. The free iodine can also be measured directly by simple absorption spectrophotometers. Also, to minimize the effect of interfering materials, several modifications of the iodometric method are given.

ASTM (2005) – Standard Test D888-05: three methods are given: titrimetric procedure –

Table 3.8: Summary of ancillary variables and their role

Type	Ancillary variable	Indication/impact
Water quality	Dissolved oxygen	Indicator of productivity and metabolic state
	Biological oxygen demand	Indicator of secondary production
	Chlorophyll a	Indicator of primary production and trophic state
	Nitrogen and phosphorus	Indicator of productivity and trophic state
	Ammonia nitrogen (NH ₃)	Indicator of agriculture or urban run-off
	Total Kjeldahl nitrogen	Indicator of productivity and trophic state
	Nitrites (NO ₂) and nitrates (NO ₃)	Indicator of secondary production (nitrifiers)
	Total phosphorus and orthophosphates	Indicator of primary production, trophic state and agriculture or urban run-off
	Water colour	Indicator of organic carbon content
	Water transparency	Indicator of organic carbon content
	Turbidity	Indicator of particulate carbon content available for transport
	Suspended solids	Indicator of particulate carbon content available for transport
	Conductivity	Used to calculate pCO ₂ using thermodynamic equations
	pH	Indicator of free CO ₂ content and used to calculate pCO ₂ using thermodynamic equations
	Alkalinity	Used to calculate pCO ₂ using thermodynamic equations
Physical water variables	Water level	Affects the drawdown zone (aquatic vs. terrestrial)
	Sediment discharge	Affects the particulate carbon stock
	Residence time	Affects sedimentation and mineralization rates
	Wave height	Affects the measurement of fluxes using a floating chamber
	Air temperature	Indicator of climate type
	Relative humidity	Indicator of climate type
	Wind direction	Indicator of wind speed and turbulence (fetch)
	Precipitation	Affects the leakage of organic material from the river basin to the aquatic system
	Atmosphere GHG concentrations	Indicator of large scale impacts of reservoir creation

high level, instrumental probe procedure and luminescence-based sensor.

3.6.1.2. Biological oxygen demand

Biochemical oxygen demand (BOD) measures the amount of oxygen consumed by micro-organisms

in decomposing organic matter in stream water. BOD also measures the chemical oxidation of inorganic matter.

WMO (1994) – No. 168, Chapter 17: one of the most commonly used measuring methods is the

dilution method; however, manometric techniques may have advantages in some circumstances. BOD is calculated from the measurement of volumetric dilution of the sample and the difference between the dissolved-oxygen concentrations of the sample before and after a five-day incubation period. The temperature should be kept at 20°C during that period, and atmospheric oxygen should be kept away from the sample, which should be stored in the dark to minimize the effect of photosynthetic action by green plants.

3.6.1.3. Chlorophyll a

Chlorophyll a is a proxy for phytoplankton abundance (abundance or biomass) of a water body. Associated with phosphorus or nitrogen concentration, it allows the determination of the trophic state of a water body.

APHA-AWWA-WEF (2005) – Standard Method 10200H: the sample is concentrated by centrifuging or filtering. The pigments are extracted from the plankton concentrate with aqueous acetone, and the optical density (absorbance) of the extract is determined with a spectrophotometer or by fluorimetric determination.

3.6.1.4. Total phosphorus and orthophosphates

Phosphorus and nitrogen are the major nutrients limiting the primary production of freshwaters. Associated with chlorophyll *a* concentration, they allow the determination of the trophic state of a water body. Phosphorus measurements are presented below. Nitrogen measurements are presented in section 3.4.2.1.5.

APHA-AWWA-WEF (2005) – Standard Method 4500-P E: phosphorus analyses entail two general procedural steps: (a) conversion of the phosphorus form of interest to dissolved orthophosphate, and (b) colorimetric determination of dissolved orthophosphate. Filtration through a membrane filter with a pore size of 0.45 µm separates dissolved from suspended forms of phosphorus.

USEPA (1993) – Method 365.1 Revision 2.0: this method covers the determination of specified forms of phosphorus in drinking, ground and surface water, and in domestic and industrial wastes. The methods are based on reactions that are specific to the orthophosphate ion. The form measured depends on the prescribed pre-treatment of the sample. The most commonly measured forms are total and dissolved phosphorus, and total and dissolved orthophosphate. Reaction with a reagent creates a complex that is reduced by ascorbic acid to an

intensely blue-coloured complex. The colour is proportional to the phosphorus concentration and is measured automatically.

3.6.1.5. Water colour

The water colour is a proxy for the estimation of the organic matter concentration.

WMO (1994) – No. 168, Chapter 17: the true colour is observed after filtration or centrifuging. Colour results from the presence of metallic ions, humus and peat materials, plankton, and industrial wastes. Colour may be obtained by visually comparing standard glass colour disks with tubes filled with the sample.

3.6.1.6. Water transparency

WMO (1994) – No. 168, Chapter 17: transparency of water is determined by its colour and turbidity. A measure of transparency can be obtained from the depth in metres at which a 20- to 30-cm Secchi disk, usually painted in black and white quadrants, disappears when slowly lowered straight down into the water. Standard block letter on white paper is sometimes used instead of the disk.

3.6.1.7. Turbidity

Turbidity is an optical measurement of suspended solids, such as clay, silt, organic matter, plankton and microscopic organisms, in a water sample.

WMO (1994) – No. 168, Chapter 17: Turbidity can be measured by nephelometric methods and be expressed in nephelometric turbidity units (NTU). Nephelometric methods measure light scattering by suspended particles. Instruments of different design, however, may give different results for the same sample. Today, electronic nephelometers are the preferred instruments for measuring turbidity.

APHA-AWWA-WEF (2005) – Standard Method 2130: turbidity was originally measured by the Jackson candle turbidimeter method but this cannot measure below 25 Jackson Turbidity Units (JTU). Thus, for samples under that value, indirect secondary methods must be used.

3.6.1.8. Suspended solids

APHA-AWWA-WEF (2005) – Standard Method 2540-D: a well-mixed sample is filtered through a weighed standard glass fibre filter and the residue retained on the filter is dried to a constant weight at 103°C to 105°C. The increase in weight of the filter represents the total suspended solids.

3.6.1.9. Conductivity

U.S. EPA (1982) – Method 120.1: This method is applicable to drinking, surface, and saline water; domestic and industrial wastes; and

acid rain (atmospheric deposition). The specific conductance of a sample is measured by using a self-contained conductivity meter, Wheatstone bridge-type, or equivalent. Samples are preferably analysed at 25°C. If not, temperature corrections are made and results reported at 25°C.

3.6.1.10. pH

Special care must be taken when measuring the pH of water since pH and $p\text{CO}_2$ are tightly linked (Figure 3.31). In the field, completely fill the bottle with the water sample and close the bottle under the water surface. The bottle's gap must be as small as possible to prevent gas escaping when the electrode is inserted into the bottle and during pH measurement (a cap with septa that maintains a hermetic seal when inserting the electrode would be better).

APHA-AWWA-WEF (2005) – Standard Methods 4500-H+: at a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. pH can be measured by the electrometric method. The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode.

U.S. EPA (1982) – Method 150.2: this method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition). The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. Samples should be analysed as soon as possible after collection, preferably in the field at the time of sampling.

3.6.1.11. Alkalinity

APHA-AWWA-WEF (2005) – Standard Methods 2320: alkalinity of water is its acid-neutralising capacity. It is the sum of all the titratable bases. Alkalinity of many surface waters is mainly a function of carbonate, bicarbonate, and hydroxide content so it is taken to indicate their concentration. Measures also may include borates, phosphates, silicates, or other bases if these are present. Alkalinity depends on the end-point pH used. pH is needed to determine the inflection points from titration curves and is the rationale for titrating to fix pH end points. The titration curve is constructed by recording sample pH with a pH meter after successive small measured additions of titrant to identify inflection points and buffering capacity. For more information, refer to the complete method.

3.6.2. Physical water variables

3.6.2.1. Water level

WMO (1994) – No. 168, Chapter 10: water level, or stage, is the elevation of the water surface of a stream, lake or other water body relative to a datum. It should be observed with a precision of 1 cm in general and of 3 mm at continuous-record gauging stations.

3.6.2.2. Sediment discharge

WMO (1994) – No. 168, Chapter 13: instantaneous samples are usually taken by trap samplers consisting of a horizontal cylinder equipped with end valves, which can be closed suddenly to trap a sample at any desired time and depth. Suspended-sediment samples are usually processed and analysed in special laboratories where, after a settling time of one to two days, the water is carefully drained off and the remaining sediment is oven-dried at a temperature of about 110°C, and weighed.

3.6.2.3. Residence time

Residence time is a measure of the average time a substance spends in a physical system. This substance could be any particle flowing with the water. Residence time is determined by the total volume of water divided by the water flow at the outlet. Total volume may be estimated by performing a bathymetric survey and water flow is measured with a flow gauge. In a reservoir, the total water flow (turbine and spillway) is used.

3.6.2.4. Wave height

Wave height is the vertical distance between the wave crest and trough; the period is the time (in seconds) it takes two successive wave crests to pass a stationary point; and the wavelength is the distance between successive crests (USACE, 1981).

To measure wave height, the significant wave height, H_s , is commonly used. $H_{1/3}$ and H_{m0} are both considered good estimates of H_s . $H_{1/3}$ is the average wave height of the one-third largest waves estimated during the sampling period by an experienced observer. Significant wave height, H_{m0} , is calculated from the wave elevation variance, which is also the zero moment, m_0 , of a non directional wave spectrum in which the summation is over all frequency bands of the non directional spectrum. An assumption for approximating significant wave height by H_{m0} is that wave spectra are narrowband. This method for determining significant wave height is suitable for nearly all purposes. More explanations for measuring wave height can be found in NOAA

(1996) – NDBC Technical Document 96-01, and WMO (1998) – No. 702.

3.6.3. Climatic conditions

3.6.3.1. Air temperature

WMO (2008) – No. 8, Part I – Chapter 2: meteorological requirements for temperature measurements relate mainly to the following: (a) the air near the Earth's surface; (b) the surface of the ground; (c) the soil at various depths; (d) the surface levels of the sea and lakes; (e) the upper air. Continuous records are desirable, especially in connection with humidity measurements. Thermometers must be shaded from the sun without restricting natural ventilation. Measurements of air temperature should be accurate to within $\pm 0.3^{\circ}\text{C}$.

3.6.3.2. Relative humidity

WMO (2008) – No. 8, Part I – Chapter 4: relative humidity is the ratio in percent of the observed vapour pressure to the saturation vapour pressure with respect to water at the same temperature and pressure. Humidity can be measured with a hygrometer. Particular requirements include: protection from direct solar radiation, atmospheric contaminants, rain and wind; and avoiding the creation of a local microclimate within the sensor housing structure or sampling device.

3.6.3.3. Wind direction

WMO (2008) – No. 8, Part I – Chapter 5: wind direction is defined as the direction from which the wind blows, and is measured clockwise from geographical ('true') north. Wind direction should be reported in degrees to the nearest 10° . Surface wind is usually measured by a wind vane, and a cup or propeller anemometer.

3.6.3.4. Precipitation

WMO (2008) – No. 8, Part I – Chapter 6: precipitation is defined as the liquid or solid products of the condensation of water vapour falling from clouds or deposited from air onto the ground. It includes rain, hail, snow, dew, rime, hoar frost and fog precipitation. The total amount of precipitation reaching the ground in a stated period is expressed in terms of the vertical depth of water (or water equivalent in the case of solid forms) to which it would cover a horizontal projection of the Earth's surface. Daily amounts of precipitation should be read to the nearest 0.2 mm and, if feasible, to the nearest 0.1 mm; weekly or monthly amounts should be read to the nearest 1 mm. Several types of gauges can be used and are chosen to reduce potential errors, such as the

effect of wind. The common observation times are hourly, three-hourly and daily, for synoptic, climatological and hydrological purposes.

3.6.3.5. Atmospheric GHG concentrations

Atmospheric GHG concentrations in the troposphere can be carried in aircraft to measure the large-scale impacts of the creation of a reservoir. Automated instrument packages can be installed on board passenger aircraft equipped with an advanced multi-probe inlet system (Schuck *et al.*, 2009). GHG samples are analysed by gas chromatography. The chromatograph is calibrated using four standard cylinders of known gas mixture (Schuck *et al.*, 2009).

3.7. Quality assurance and quality control

The International Organization for Standardization (ISO) provides guidance on the preservation and handling of water samples, on quality assurance of environmental water sampling and handling, and analytical quality control for chemical and physicochemical water analysis.

3.7.1. General considerations

A Quality Assurance/Quality Control (QA/QC) programme contributes to improve transparency, consistency, comparability, completeness, and confidence in any study programme.

A quality assurance and quality control (QA/QC) programme for the measurement of GHG emissions (diffusion, bubbling and GHG export downstream of dams), and carbon stock will include the following points: establishment of a QA/QC management plan; instrument calibration; prevention of samples contamination and deterioration to ensure good measurements; data validation (including identification of bias or systematic error, precision of data or closeness); and a posteriori analysis and report.

IPCC (2000, 2006) provides a good definition of QC/QA system for national greenhouse gas emission inventories; detailed procedures are given in the guides *Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories* (Chapter 8), and *2006 IPCC Guidelines for National Greenhouse Gas Inventories* (Volume 1, Chapter 6). The IPCC defines the terms as follow:

- Quality Control (QC) is a system of routine technical activities to measure and control the quality of the inventory as it is being

developed. QC activities include general methods such as accuracy checks on data acquisition and calculations and the use of approved standardised procedures for emission calculations, measurements, estimating uncertainties, archiving information and reporting.

- Quality Assurance (QA) activities include a planned system of review procedures conducted by personnel not directly involved in the inventory compilation/development process. Reviews verify that data quality objectives were met; ensure that the inventory represents the best possible estimates of emissions and sinks given the current state of scientific knowledge and data available; and support the effectiveness of the QC programme.

Other documents published by international agencies; e.g., Environment Protection Agency (U.S.A.), Regional Environmental Center (Europe), or Environment Canada (Canada), will also include explained procedures of QA/QC. Each country and each study should develop its own QA/QC programme. QA/QC programmes will differ between studies based on the budget available, amount of data to be collected, type of instruments used, or other factors.

For aquatic sampling, a lot of information about QA/QC can be found in the *Standard Method for the Examination of Water and Wastewater (APHA-AWWA-WEF, 2005)* in section 1020.

For meteorological data sampling, refer to the *Guide to Meteorological Instruments and Methods of Observation; Part III (WMO, 2008)*.

For hydrological data sampling: *Guide to Hydrological Practices – Data Acquisition and Processing, Analysis, Forecasting and Other Applications; Chapter 22 (WMO, 1994)*.

Samples for laboratory analysis

The following items should be considered when samples are collected for laboratory analysis (field laboratory or accredited laboratory):

1. Collection: samples must be collected and properly handled, avoiding contamination (for example by emanation of gas from the boat engine while measuring with a static chamber), and losses of compounds (e.g., microbial degradation, sample drying, oxidation, volatilisation).
2. Replicate measurements should be analysed. The number of replicates can vary depending on the type of sample and the scope.

3. Conservation: follow the pre-treatment, conservation procedures (e.g., conservation agent, temperature), and analyse delay of each variable.
4. Analysis: The right method should be identified; e.g., the method can change for the same variable depending on the concentration.
5. Internal controls from the laboratory: different controls can be applied to ensure the reliability of the results:
 - field blank;
 - use three to six measurement standards covering the range of the measures to generate the standard curve;
 - analyse method blanks regularly through the sample analyses (one sample for each 20 samples);
 - use fortified samples (one sample for each 10 samples);
 - analyse in triplicate some samples regularly to check the repeatability of the analyses (one sample for each 10 samples);
 - use control samples that are coming or from another laboratory, or of a certified organisation;
 - measure samples near the detection limit.
6. Comparison of results between two different laboratories.
7. Sending ghost samples: duplicate samples that are identified differently.

3.7.2. Instruments

1. Testing, calibrating with standards and intercomparison of instruments are basic steps that should be included in a QA programme.
2. The operator of the instrument must be trained and have the required competence in making the analysis.
3. Each instrument's maintenance specifications need to be followed. As a general rule, most instruments need to be zeroed, calibrated and warmed up before use. Zeroing and calibration can be performed by the user or by the manufacturer, depending on the instrument. The warm-up period can vary greatly between instruments.

3.8. References

- Abe, D. S., Adams, D. D., Sidagis-Galli, C., Sikar, E., Tundisi, J. G. 2005. Sediment greenhouse gases (CH₄ and CO₂) in the Lobo-Broa Reservoir, São Paulo State, Brazil: Concentrations and diffuse emission fluxes for carbon budget considerations. *Lakes & Reservoirs Research and Management*, 10: 201–209.
- Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Santos, M. A., and Matvienko, B. 2005. Carbon dioxide and methane emissions and the carbon budget of a 10-years old tropical reservoir (Petit-Saut, French Guiana). *Global Biogeochem. Cycles* 19: GB 4007, doi:10.1029/2005GB002457.
- Adams, D. D. 1991. Gas composition of Hamilton Harbor sediments: changes during the 1980-1990 decade. Canada Centre for Inland Waters, National Water Research Institute, Burlington, Ontario, Canada, Internal Report.
- Adams, D. D. 1994. Sampling sediment pore water. Edited by Mudroch A. and MacKnight S. D. *Handbook of Techniques for Aquatic Sediments Sampling*. 2nd ed. CRC Press, Boca Raton, p.171–202.
- Adams, D. D., Baudo, R. 2001. Gases (CH₄, CO₂ and N₂) and pore water chemistry in the surface sediments of Lake Orta, Italy: Acidification effects on C and N gas cycling. *J. Limnol.*, 60: 79–90.
- Adams, D. D. 2005. Diffusive flux of greenhouse gases: methane and carbon dioxide at the sediment-water interface of some lakes and reservoirs of the world. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p.119.
- American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF). 2005. *Standard Methods for the Examination of Water and Wastewater*, 21st Edition. Edited by Andrew D. Eaton (AWWA, Chair), Lenore S. Clesceri (WEF), Eugene W. Rice (APHA), Arnold E. Greenberg (deceased, APHA). Centennial edition.
- American Society for Testing and Materials (ASTM). 1997. *ASTM Standards on Environmental Sampling*. 2nd edition. Edited by RA Storer.
- Anderson, C.B. 2002. Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems. *Journal of Geoscience Education*. Vol. 50, No. 4, p. 389–403.
- Araujo A.C., Nobre A.D., Kruijt B., Culf A.D., Stefani P., Elbers J., Dallarosa R., Randow C., Manzi A.O., Valentini R., Gash J.H.C., Kabat P. 2002. Dual tower long-term study of carbon dioxide fluxes for a central Amazonian rain forest: the Manaus LBA site. *J Geophys Res Atmos* 107(D20):8090. DOI 10.1029/ 2001JD000676.
- Baldocchi, D.D. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. *Global Change Biology*, 9(4): 479–492.
- Banerjee, S., and MacIntyre, S. 2004. The air-water interface: Turbulence and scalar exchange, in *Advances in Coastal and Ocean Engineering*, edited by P. L. F. Liu, pp. 181–237, World Sci., Hackensack, N. J.
- Barth, J. A. C, Veizer, J. and Mayer, B. 1998. Origin of particulate organic carbon in the upper St. Lawrence: isotopic constraint, *Earth Planet. Sci. Lett.*, 162, 111–121.
- Bastien, J. 2005. Impacts of Ultraviolet Radiation on Aquatic Ecosystems: Gas Emissions and Implications for Hydroelectric Reservoirs. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p 509-527.
- Bastien, J., Côté, A. and Tremblay, A. 2007. *Aménagement hydroélectrique de l'Estmain-1 – Étude des flux de gaz à effet de serre – Résultats été 2007*. Joint report from Environnement Illimité inc. and Hydro-Québec Production, Direction Barrages et Environnement. 49 p. and appendices.
- Bastviken, D., Cole, J., Pace, M., and Tranvik, L. 2004. Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Glob. Biogeochem. Cycle*, 18, Gb4009. doi: 10.1029/2004GB002238.
- Bernier, P., Hanson, P.J. and Curtis, P.S. 2008. Measuring litterfall and branchfall. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 7. Ed. CM Hoover. Springer, New York. 240 p.
- Bertilsson, S. and Tranvik, L.J. 2000. Photochemical transformation of dissolved organic matter in lakes. *Limnology and Oceanography*, Vol 45(4), pp. 753 762.

- Bisutti, I.; Hilke, I.; Raessler, M. 2004. Determination of total organic carbon – an overview of current methods; Trends in Analytical Chemistry, vol. 23, n° 10-11.
- Blais, A-M, Bastien, J. and Tremblay, A. 2007. *Aménagement hydroélectrique de l'Eastmain-1 – Étude des flux de gaz à effet de serre – Résultats 2006*. Joint report from Environnement Illimité inc. and Hydro-Québec Production, Direction Barrages et Environnement. 80 p. and appendices.
- Borges, A. V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G. and Frankignoulle, M. 2004a. Gas transfer velocities of CO₂ in three European estuaries (Randers Fjord, Scheldt and Thames). *Limnology and Oceanography*, 49:1630–641.
- Borges, A. V., Vanderborcht, J.P., Schiettecatte, L.-S., Gazeau, F., Ferron-Smith, S., Delille, B. and Frankignoulle, M. 2004b. Variability of the gas transfer velocity of CO₂ in a macrotidal estuary (the Scheldt). *Estuaries*, 27:593–603.
- Bradford, J.B. and Ryan, M.G. 2008. Quantifying soil respiration at landscape scales. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 11. Ed. CM Hoover. Springer, New York. 240 p.
- Bubier, J.L., Moore, T.R. and Crosby, G.. 2006. Fine-scale vegetation distribution in a cool temperate peatland. *Canadian Journal of Botany*. 84: 910–923.
- Burton, A.J. and Pregitzer, K.S. 2008. Measuring forest floor, mineral soil, and root carbon stocks. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 10. Ed. CM Hoover. Springer, New York. 240 p.
- Chojnacky, D.C. and Milton, M. 2008. Measuring carbon in shrubs. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 5. Ed. CM Hoover. Springer, New York. 240 p.
- Christensen, T. R., Panikov, N., Mastepanov, M., Joabsson, A., Stewart, A., Oquist, M., Sommerkorn, M., Reynaud, S., and Svensson, B. 2003. Biotic controls on CO₂ and CH₄ exchange in wetlands – a closed environment study, *Biogeochemistry*, 64: 337–354.
- Cole, J.J. 1999. Aquatic Microbiology for Ecosystem Scientists: New and Recycled Paradigms in Ecological Microbiology. *Ecosystems*, Vol 2, pp. 215-225.
- Cole, J.J. and Caraco, N.F. 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆. *Limnology and Oceanography*. Vol 43, No. 4. p: 647–656.
- Corin N, Backlung, P, and Kulovaara M. 1996. Degradation products formed during UV-irradiation of humic waters. *Chemosphere*, Vol. 33, pp. 245-255.
- Crusius, J. and Wanninkhof, R. 2003. Gas transfer velocities measured at low wind speed over a lake. *Limnology and Oceanography*. Vol. 48. No. 3. p. 1010–1017.
- Curtis, P.S. 2008. Estimating aboveground carbon in live and standing dead trees. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 4. Ed. CM Hoover. Springer, New York. 240 p.
- Curtis, P.S., Hanson, P.J., Bolstad, P., Barford, C., Randolph, J.C., Schmid, H.P. and Wilson, K.B. 2002. Biometric and eddy-covariance based estimates of annual carbon storage in five eastern North American deciduous forests. *Agricultural and Forest Meteorology*. 113: 3–19.
- Dahlén J., Bertilsson, S. and Pettersson, C. 1996. Effects of UV-A irradiation on dissolved organic matter in humic surface waters. *Environment International*, Vol 22, No 5, pp. 501-506.
- Davies-Colley, R.J. and Vant, W.N. 1987. Absorption of Light by Yellow Substance in Freshwater Lakes. *Limnology and Oceanography*, Vol 32, Issue 2, pp. 416 425.
- De Langre, E. 2008. Effects of Wind on Plants. *Annual Review of Fluid Mechanics*. 40: 141–168.
- Dean, W. 1974. Determination of Carbonate and Organic Matter in Calcareous Sediments and Sedimentary Rocks by loss on Ignition: Comparison with other Methods. *Journal of Sedimentary Petrology*. Vol. 44, no. 1, pp. 242-248.
- Dean, W. 1999. The Carbon Cycle and Biogeochemical Dynamics in Lake Sediments . *Journal of paleolimnology*. Vol. 21 (4) pp. 375-393.
- Del Giorgio, P. A., Cole, J. J., Caraco, N. F. and Peters, R. H. 1999. Linking planktonic biomass and metabolism to net gas fluxes in morthern temperate lakes. *Ecology*, 80(4): 1422–1431.
- Demarty M., Bastien, J., Tremblay, A., Hesslein, R. and Gill, R. 2009. Greenhouse Gas Emissions from Boreal Reservoirs in Manitoba and Québec, Canada, Measured with Automated Systems. *Environmental Science & Technology*. Vol 43, pp. 8908-8915.

- Ellert, B.H., H.H. Janzen, A.J. Vanden Bygaart and E. Bremer. 2008. Measuring Change in Soil Organic Carbon Storage. Chap. 3 in *Soil sampling and methods of analysis* edited by M.R. Carter and E.G. Gregorich. Canadian Society of Soil Science, CRC Press.
- Environment Canada. 2002a. Sediment Sampling Guide for Dredging and Marine Engineering Projects in the St. Lawrence River. Volume 1, Planning Guidelines. Environment Canada, Environmental Protection Branch, Quebec Region Technological Innovation and Industrial Sectors Section. Report 101 pages.
- Environment Canada. 2002b. *Sediment Sampling Guide for Dredging and Marine Engineering Projects in the St. Lawrence River. Volume 2, Field Operations Manual*. Environment Canada, Environmental Protection Branch, Quebec Region Technological Innovation and Industrial Sectors Section. Report 103 pages.
- Erickson III, D.J., R.G. Zepp, E. Atlas, 2000. Ozone depletion and the air-sea exchange of greenhouse and chemically reactive trace gases. *Chemosphere*. Global Change Science 2, pp. 137-149.
- Ertel J.R. 1990. Photooxidation of dissolved organic matter: An organic geochemical perspective. In: Effects of solar radiation of biogeochemical dynamics in aquatic environments. Woods Hole Oceanography. Technical Report WHOI-90-90. pp.79-81.
- Falge, E., D. Baldocchi, R. Olson, P. Anthoni, M. Aubinet, C. Bernhofer, G. Burba, R. Ceulemans, R. Clement, H. Dolman, A. Granier, P. Gross, T. Grunwald, D. Hollinger, N. O. Jensen, G. Katul, P. Keronen, A. Kowalski, C. T. Lai, B. E. Law, T. Meyers, J. Moncrieff and E. Moors. 2001. Gap filling strategies for defensible annual sums of net ecosystem exchange. *Agricultural and Forest Meteorology*, 107(1), 43–69.
- Forster, P., V. Ramaswamy, P. Artaxo, T. Bernsten, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland. 2007. Changes in Atmospheric Constituents and in Radiative Forcing. In *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Edited by S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller. Cambridge and New York: Cambridge University Press.
- Frankignoulle, M., I. Bourge and R. Wollast. 1996. Atmospheric CO₂ fluxes in a highly polluted estuary (The Scheldt). *Limnol. Oceanogr.*, 41:365-369.
- Galy-Lacaux, C., Delmas, R., Jambert, C., Dumestre, J. F., Labroue, L., Richard, S., and Gosse, P. 1997. Gaseous emissions and oxygen consumption in hydroelectric dams: A case study in French Guiana. *Global Biogeochem. Cycles* 11: 47 –483.
- Gastonguay L, Champagne, G.Y., Ladouceur, M. and Lacasse, R. 1995. Dosage électrochimique des substances humiques dans les eaux des réservoirs hydroélectriques. Rapport IREO-95-010, Hydro-Québec, Montréal.
- Goulden, M.L., Munger, J.W., Fan, S.M., Daube, B.C. and Wofsy S.C. 1996. Measurements of carbon sequestration by long-term eddy covariance: Methods and a critical evaluation of accuracy. *Global Change Biology*, 2(3): 169–182
- Groves, R.M. 1989, Survey errors and survey costs, Wiley, New York.
- Groves, R.M. 2004, Survey methodology, J. Wiley, Hoboken, NJ.
- Gregoire T.G., Valentine, H.T. and Furnival, G.M. 1995. Sampling methods to estimate foliage and other characteristics of individual trees. *Ecology*, Vol. 76(4), pp 1181–1194.
- Guérin, F. and G. Abril. 2007. Significance of pelagic aerobic methane oxidation in the methane and carbon budget of a tropical reservoir. *Journal of Geophysical Research*. 112: G03006, doi: 10.1029/2006JG000393.
- Guérin F., Abril G., Tremblay A. and Delmas R. 2008. Nitrous oxide emissions from tropical hydroelectric reservoirs. *Geophysical Research Letters* 35, doi:10.1029/2007GL033057.
- Hansen, M.H. 1953, Sample survey methods and theory, Wiley, New York.
- Häder D.P. 1997. The effects of ozone depletion on aquatic ecosystems. Academic Press, Texas.
- Hashmonay R.A. and Crosson E. 2009. AIR-130 : Emission Measurement Techniques for Greenhouse Gases (GHGs) from Area and Fugitive Sources. 140 p.
- Hélie, J.F. 2004. Géochimie et flux de carbone organique et inorganique dans les milieux aquatiques de l'est du Canada: exemples du Saint-Laurent et du réservoir Robert-Bourassa – Approche isotopique. PhD. thesis presented to Université du Québec à Chicoutimi, January 2004.

- Hendzel, L.L., Matthews, C.J.D., Venkiteswaran, J.J., St. Louis, V.L., Burton, D., Joyce, E.M. and Bodaly, R.A. 2005. Nitrous oxide fluxes in three experimental boreal forest reservoirs. *Environmental science & technology*, vol. 39, no12, pp. 4353–4360 [8 page(s) ISSN 0013-936X.
- Hessen, D.O. 2002. UV radiation and arctic ecosystems. Springer, Berlin.
- Hollinger, D.Y. 2008. Meteorological measurements. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 3. Ed. CM Hoover. Springer, New York. 240 p.
- Hoover, C.M. 2008. *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Springer, New York. 240 p.
- Huttunen, J. T., Lappalainen, K. M., Saarijärvi, E., Vaisanen, T. and Martikainen, P. J. 2001. A novel sediment gas sampler and a subsurface gas collector used for measurement of the ebullition of methane and carbon dioxide from a eutrophied lake. *The Science of the Total Environment*, 266: 153–158.
- Huttunen, J.T., Väisänen, T.S., Heikkikinen, M., Hellsten, S. Nykänen, H., Nenonen, O. and Martikainen, P.J. 2002. Fluxes of CH₄, CO₂, and N₂O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland. *Global Biogeochem. Cycle*. 16: 1–17.
- Intergovernmental Panel on Climate Change (IPCC). 2000. IPCC Good Practice Guidance and Uncertainty management in National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Programme. Published: IGES, Japan.
- Intergovernmental Panel on Climate Change (IPCC). 2003. Good Practice Guidance for Land Use, Land Use Change and Forestry. Punman J., Geytarsky M., Hiraishi T., Krug T., Kruger D., Pipatti R., Buendia L., Miwa K., Ngara T., Tanabe K., Wagner F. (eds). Published by IGES, Japan.
- Intergovernmental Panel on Climate Change (IPCC). 2006. *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. Prepared by the National Greenhouse Gas Inventories Programme. Edited by H.S. Eggleston, L. Buendia, K. Miwa, T. Ngara and K. Tanabe. Published: IGES, Japan.
- Jenkins J.C., Chojnacky D.C., Heath L.S., and R.A. Birdsey. 2003. *Comprehensive database of diameter-based biomass regressions for North American tree species*. Newton Square, PA: USDA Forest Service. GTR-NE-319.
- Kampbell, D.H. and Vandegrift, S.A. 1998. Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *Journal of Chromatographic Science* 36: 253–256.
- Karberg, N.J., Scott, N.A. and Giardina, C.P. 2008. Methods for estimating litter decomposition. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 8. Ed. C.M. Hoover. Springer, New York. 240 p.
- Keller M. and Stallard R.F. 1994. Methane emissions by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research* 99: 8307–8319.
- Kish, L. 1995, Survey sampling, Wiley classics library edn, Wiley, New York.
- Kljun, N., Calanca, P., Rotach, M.P., & Schmid, H.P. 2004. A simple parameterisation for flux footprint predictions. *Boundary-Layer Meteorology*, 112, 503–523.
- Kobashi, H. and Kato, T. 2007. High-resolution mapping of the seasonal changes in leaf area index and above ground biomass in Qinghai-Tibetan Plateau, China. *Proceedings of the Asian Conference on Remote Sensing (ACRS)*.
- Kolb, B. and Ettre, L.S. 2006. *Static Headspace-Gas Chromatography, Theory and Practice*. Second Edition. John Wiley & Sons. 349 p.
- Kolka R., Weishampel, P. and Froberg, M. 2008. Measurement and importance of dissolved organic carbon. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 13. Ed. CM Hoover. Springer, New York. 240 p.
- Kremer, J. N., Nixon, S. W., Buckley, B. and Roques P. 2003. Technical note: Conditions for using the floating chamber method to estimate air-water gas exchange. *Estuaries* 26, 985–990.
- Kutsch, W.L, Staack, A., Wotzel, J., Middelhoff, U. and Kappen, L. 2001. Field measurements of root respiration and total soil respiration in an alder forest. *New Phytologist* 150: 157–168.
- Kuzyakov, Y. 2006. Sources of CO₂ efflux from soil and review of partitioning methods. *Soil Biology and Biochemistry* 38: 425–448.
- Kuzyakov, Y. and Larionova, A.A. 2005. Root and rhizomicrobial respiration: A review of approaches to estimate respiration by autotrophic and heterotrophic organisms in soil. *Journal of Plant Nutrition and Soil Science* 168: 503–520.
- Lambert, M. and Fréchette, J.-L. 2005. Analytical techniques for measuring fluxes of CO₂ and CH₄

from hydroelectric reservoirs and natural water bodies. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p. 37–60.

Lee, X., Massman, W. and Law, B. 2004. *Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis*. Springer-Verlag.

Levy, P. & Lemeshow, S. 1999, *Sampling of populations: methods and applications*, Wiley, New York.

Lide, D.R. 2007. *CRC Handbook of Chemistry and Physics*, 88th edition. CRC Press, New York.

Macintyre, S., Wanninkhof, R. and Chanton, J.P. 1995. Trace gas exchange across the air-water interface in freshwater and coastal marine environments. Chapter 3, p. 52–97. In *Freshwater and coastal marine environments*. P.A. Matson & Harriss (eds). Blackwell Science. 394 p.

Matthews, C.J.D., Saint-Louis, V.L. and Hesslein, R.H. 2003. Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces. *Environ. Sci. Technol.* 37, 772–780.

McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E., and Wuest, A. 2006. Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere? *Journal of Geophysical Research*, Vol. 111, C09007.

McNair H.M. and Miller, J.M. 2009. *Basic Gas Chromatography*. 2nd edition. Published by John Wiley and Sons. 233 p.

Meyers P.A. and Ishiwatari, R. 1993. Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. Volume 20, Issue 7, pp. 867–900.

Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP). 2008. Guide d'échantillonnage à des fins d'analyses environnementales, Cahier 5, Échantillonnage des sols. Published by Centre d'expertise en analyse environnementale du Québec (CEAEQ), Québec, 59 p.

Moncrieff, J.B., Mahli, Y. And Leuning, R. 1996. 'The propagation of errors in long term measurements of land atmosphere fluxes of carbon and water', *Global Change Biology*, 2, 231–240

Moore T.R., Bubier, J.L., Frolking, S.E., Lafleur, P.M. and Roulet, N.T. 2002. Plant biomass and production and CO₂ exchange in an ombrotrophic bog. *Journal of Ecology*. 90: 25–36.

Moran M.A. and Hodson, R.E. 1990. Bacterial production on humic and nonhumic components of dissolved organic carbon. *Limnology & Oceanography* 35(8), pp. 1744–1756.

Morel, F.M.M. 1982. *Principles of aquatic chemistry*. John Wiley & Sons, New York, 446 p.

Morgenstern K., Black T.A., Humphreys E.R., Griffis T.J., Drewitt G.B., Cai T, Nesic Z., Spittlehouse D.L. and Livingston N.J. 2004. Sensitivity and uncertainty of the carbon balance of a Pacific Northwest Douglas-fir forest during an El Niño/La Niña cycle. *Agricultural and Forest Meteorology*, 123: 201–219.

Mudroch, A., Macknight, S. 1994. *Handbook of Techniques for Aquatic Sediments Sampling*. 2nd ed. CRC Press, Boca Raton, 236p.

NOAA. 1996. *Nondirectional and Directional Wave Data Analysis Procedures – NDBC Technical Document 96-01*. Stennis Space Center, U.S. DEPARTMENT OF COMMERCE. Edited by Ronald Brown, U.S. DEPARTMENT OF COMMERCE, Dr. D. James Baker, National Oceanic and Atmospheric Administration, and Jerry C. McCall, National Data Buoy Center. 37 pp. www.ndbc.noaa.gov/wavemeas.pdf

Obernosterer I., Reitner, B. and Herndl, G.J. 1999. Contrasting Effects of Solar Radiation on Dissolved Organic Matter and Its Bioavailability to Marine Bacterioplankton. *Limnology and Oceanography*, Vol 44, Issue 7, pp 1645–1654.

Ostrovsky, I. 2003 Methane bubbles in lake Kinneret: quantification and temporal and spatial heterogeneity. *Limnology and Oceanography*, vol. 48, N.3.

Ostrovsky, I.; D. F. McGinnis, L. Lapidus, and Eckert, W. 2008. Quantifying gas ebullition with echosounder: the role of methane transport by bubbles in a medium-sized lake. *Limnology and Oceanography: Methods* 6, 2008, 105–118.

Paré D., Boutin, R., Larocque, G.R. and Raulier, F. 2006. Effect of temperature on soil organic matter decomposition in three forest biomes of eastern Canada. *Canadian Journal of Soil Science*. 86: 247–256

Pattey, E., Edwards, G., Strachan, I.B., Desjardins, R.L., Kaharabata, S. and Wagner Riddle, C. 2006. Towards standards for measuring greenhouse gas flux from agricultural fields using instrumented towers. *Canadian Journal of Soil Science* 86: 373–400.

- Petterson C., Rahm, L., Allard, B. and Borén, H. 1997. Photodegradation of Aquatic Humic Substances: an important Factor for the Baltic Carbon Cycle. *Boreal Environment Research* (2), pp. 209-215.
- Prairie, Y. 2009. Sampling protocol for greenhouse gas emissions from reservoirs. Personal communication. 6p.
- Prairie Y.T., Bird D.F., Cole J. 2002. The summer metabolic balance in the epilimnion of southeastern Quebec lakes. *Limnology and Oceanography*, 47(1), 2002, PP.316-321.
- Ramos, F. M., Lima, I. B. T., Rosa, R. R., Mazzi, E. A., Carvalho, J. C., Rasera, M., Ometto, J., Assireu, A. T. and Stech, J. L. 2006. Extreme event dynamics in methane ebullition fluxes from tropical reservoirs. *Geophysical Research Letters* 33(21). DOI: 10.1029/2006GL027943.
- Rau, G. 1978. Carbon-13 Depletion in a Subalpine Lake: Carbon Flow Implications, *Science*, 201, 901–902.
- Reche I., Pace, M.L. and Cole, J. 1999. Relationship of trophic and chemical conditions to photobleaching of dissolved organic matter in lake ecosystems. *Biogeochemistry*, Vol 44, pp 259-280.
- Rocha, H.R., Freitas H., Rosolem, R., Juarez, R., Tannus, R.N., Ligo, M.V., Cabral, O.M.R., Silva Dias, M.A.F. 2002. Measurements of CO₂ exchange over a woodland savanna (Cerrado Sensus stric- to) in southeast Brasil. *Biota Neotropica* 2(1)
- Rocha, H.R., Goulden, M.L., Miller, S.D., Menton, M.C., Pinto, L.D.V.O., Freitas, H.C., Figueira, A.M.S. 2004. Seasonality of water and heat fluxes over a tropical forest in eastern Amazonia. *Ecol Appl* Suppl 14(4): S22–S32.
- Rochette, P. and Bertrand, N.. 2008. Soil-Surface Gas Emissions. In *Soil Sampling and Methods of Analysis*, pp. 851 – 862, edited by Martin R. Carter and Gregorich, E. G. [Pinawa, Manitoba]: Canadian Society of Soil Science ; Boca Raton, FL: CRC Press, 2008.
- Santos, M.A., Matvienko, B., Rosa, L.P., Sikar, E. and Santos, E. O. 2005. Gross Greenhouse Gas Emissions from Brazilian Hydro Reservoirs. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p. 267–291.
- Schmid, H.P. 1994. Source Areas for Scalars and Scalar Fluxes. *Boundary-Layer Meteorology*, 67(3): 293–318.
- Schmid, H.P. 2002. Footprint modeling for vegetation atmosphere exchange studies: a review and perspective. *Agricultural and Forest Meteorology*, 113(1-4): 159–183.
- Schmidt U. and Conrad, R. 1993. Hydrogen, Carbon Monoxide, and Methane Dynamics in Lake Constance. *Limnology and Oceanography*, Vol 38, Issue 6, pp 1214 1226.
- Schuck, T.J., Brenninkmeijer, C.A.M., Slemr, F., Xueref-Remy, I. and Zahn, A. 2009. Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft. *Atmospheric Measurement Techniques*. 2: 449–464.
- Scott, N.A. and Brown, S.. 2008. Measuring the decomposition of down dead-wood. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 9. Ed. CM Hoover. Springer, New York. 240 p.
- Simon, A., Bingner, R.L., Langendoen, E.J., Alonso, C.V. 2002. Actual and Reference Sediment Yields for the James Creek Watershed - Mississippi. USDA-ARS National Sedimentation Laboratory Research Report. no. 31., pp. 185.
- Sobek, S. 2006. A Carbon Budget of a Small Humic Lake: An Example of the Importance of Lakes for Organic Matter Cycling in Boreal Catchments. *Ambio*. Vol. 35, Issue 8 pp. 469–475.
- Somer. 1992. *Guide méthodologique des relevés de la qualité de l'eau*. Rapport de la Société multidisciplinaire d'études et de recherches de Montréal pour Hydro-Québec. 79 p and appendices.
- Sorenson, S. 1909. *Über die Messung und die Bedeutung der Wasserstoff ionen Konzentration bei Enzymatischen Prozessen*. *Biochem. Z.* 21:131.
- Stumm, W. and Morgan, J.J. 1996. *Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters*, 3rd edition. John Wiley & Sons, New York, 780 p.
- Svensson J.M. 1998. Emission of N₂O, nitrification and denitrification in a eutrophic lake sediment bioturbated by *Chironomus plumosus*. *Aquatic Microbial Ecology* 14(3):289-299.
- Tang J., Qi, Y., Xu, M., Misson, L. and Goldstein A.H. 2005. Forest thinning and soil respiration in a ponderosa pine plantation in the Sierra Nevada. *Tree Physiology* 25: 57-66.

Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y. 2002. Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects, *Deep-Sea Res.*, Part II, 49(9–10): 1601–1622.

Ter-Mikaelian, M.T. and Korzukhin, M.D. 1997. Biomass equations for sixty-five North American tree species. *Forest Ecology and Management*, 97: 1–24.

Thérien, N. and K. Morrison. 2005. Production of GHG from the decomposition of in vitro inundated phytomass and soil. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p. 315–338.

Tremblay, A., Therrien J., Hamlin B., Wichmann E And L.J. Ledrew. 2005. GHG Emissions from Boreal Reservoirs and Natural Aquatic Ecosystems. In: Tremblay, A., Varfalvy, L., Roehm, C. and Garneau, M. (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments. Environmental Science Series*, Springer, New York, p. 209–232.

Tremblay, A., Varfalvy, L., Lambert, M. 2005. Greenhouse gas emissions from hydroelectric reservoirs in Canada. In: Santos, M. A. and Rosa, L. P. 2005. *Global Warming and Hydroelectric Reservoirs. COPPE/UFRJ; Eletrobras*, Rio de Janeiro, p. 175–183.

Tremblay, A. and J. Bastien. 2009. Greenhouse Gases Fluxes from a New Reservoir and Natural Water Bodies in Québec, Canada. *Verh. Internat. Verein. Limnol.* Vol 30, Part 6, p. 866–869.

Tundisi, J.G., M.A. Santos and C.F.S. Menezes. 2006. Tucuruí Reservoir: Experience and Lessons Learned Brief.

UNESCO/IHA. 2009. The UNESCO/IHA Measurement Specification Guidance for Evaluating the GHG Status of Man-Made Freshwater Reservoirs. Edition 1 – June 2009.

UNESCO/IHA. 2008. Assessment of the GHG Status of Freshwater Reservoirs – Scoping Paper. April 2008.

United Nations Framework Convention on Climate Change (UNFCCC). 2007. Proposed new baseline and monitoring methodologies for estimating GHG emissions from the Bumbuna Hydroelectric Project, Sierra Leone, CDM-NM00121.

United Nations Framework Convention on Climate Change (UNFCCC). 2009. Draft general guidelines on sampling and surveys. EB 47 report, annex 27, CDM – Executive Board. 28 May 2009.

United States Department of Agriculture (USDA). 2006. Forest Inventory and Analysis National Core Field Guide. Volume 1, Field Data Collection Procedures for Phase 2 Plots.

United States Environmental Protection Agency (U.S. EPA). 1982. pH, Continuous Monitoring (Electrometric) – Method 150.2. US Environmental Protection Agency. [On line (july 2010): <http://www.epa.gov/waterscience/methods/method/>]

United States Environmental Protection Agency (U.S. EPA). 1982. Conductance (Specific Conductance, umhos at 25°C) – Method 120.1. US Environmental Protection Agency. [On line (july 2010): <http://www.epa.gov/waterscience/methods/method/>]

United States Environmental Protection Agency (U.S. EPA). 1993. Determination of Ammonia Nitrogen by Semi-Automated Colorimetry – Method 350.1 Revision 2.0. Edited by James W. O'Dell, Inorganic Chemistry Branch, Chemistry Research Division. US Environmental Protection Agency. [On line (july 2010): <http://www.epa.gov/waterscience/methods/method/>]

United States Environmental Protection Agency (U.S. EPA). 1993. Determination Of Nitrate-Nitrite Nitrogen By Automated Colorimetry – Method 353.2 Revision 2.0. Edited by James W. O'Dell, Inorganic Chemistry Branch, Chemistry Research Division. US Environmental Protection Agency. [On line (july 2010): <http://www.epa.gov/waterscience/methods/method/>]

United States Environmental Protection Agency (U.S. EPA). 1993. Determination Of Phosphorus By Semi-Automated Colorimetry – Method 365.1 Revision 2.0. Edited by James W. O'Dell, Inorganic Chemistry Branch, Chemistry Research Division. US Environmental Protection Agency. [On line (july 2010): <http://www.epa.gov/waterscience/methods/method/>]

USACE. 1981. *Low cost shore protection: A guide for engineers and contractors – Section 54*. US Army Corps of Engineers. US Government Printing Office, Washington, DC, 162 pp.

Valentine H.T., Gove, J.H., Ducey, M.J., Gregoire, T.G. and Williams, M.S. 2008. Estimating the carbon in coarse woody debris with perpendicular distance sampling. In *Field Measurements for*

Forest Carbon Monitoring: A Landscape-Scale Approach. Chapter 6. Ed. CM Hoover. Springer, New York. 240 p.

Vesala T., Huotari, J., Rannick, U., Suni, T., Smolander, S., Sogachev, A., Launiainen S. and Ojala, A. 2006. Eddy covariance measurements of carbon exchange and latent and sensible heat fluxes over a boreal lake for a full open-water period. *Journal of Geophysical Research*, 111, D11101, doi: 10.1029/2005JD006365.

Vodacek A., Blough, N.V., Degrandpre, M.D., Peltzer, E.T. and Nelson, R.K. 1997. Seasonal Variation of CDOM and DOC in the Middle Atlantic Bight : Terrestrial Inputs and Photooxidation. *Limnology and Oceanography*, Vol 42, Issue 4, pp 674-686.

Wang, Z., Zeng, D. and Patrick Jr., W.H.. 1996. Methane emissions from natural wetlands. *Environmental Monitoring and Assessment*, 42(2): 143–161.

Wanninkhof, R., 1992. Relationship between Wind Speed and Gas Exchange Over the Ocean. *Journal of Geophysical Research*, Vol. 97, No. C5 (1992), p.7373-7382.

Weishampel, P. and Kolka, R.. 2008. Measurement of methane fluxes from terrestrial landscapes using static, non-steady state enclosures. In *Field Measurements for Forest Carbon Monitoring: A Landscape-Scale Approach*. Chapter 12. Ed. CM Hoover. Springer, New York. 240 p.

Weiss, R.F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* 2, 203–215.

Weiss, R.F. 1981. Determinations of carbon dioxide and methane by dual catalyst flame

ionisation chromatography and nitrous oxide by electron capture chromatography. *Journal of Chromatographic Science*. Vol. 19, p: 611–616.

Wetzel, R.G. 1975. *Limnology*. Saunders, Philadelphia.

Wetzel R.G. 1995, Death, detritus and energy flow in aquatic ecosystems. *Freshwater Biology*, 33: 83-89.

Wetzel, R.G. 2001. *Limnology. Lake and River Ecosystems*. Third Ed. Academic Press, San Diego. xvi, 1006 pp. ISBN 0-12-744760-1.

Willard, H.H., Merritt Jr., L.L., Dean, J.A. and Settle Jr., F.A. 1988. *Instrumental Methods of Analysis*. 7th edition. Wadsworth Publishing Company. 895 p.

Williamson, C.E., Stemberger, R.S., Morris, D.P., Frost, T.M. and Paulsen, S.G. 1996. Ultraviolet Radiation in North American Lakes : Attenuation Estimates from DOC Measurements and Implications for Plankton Communities. *Limnology and Oceanography*, Vol 41, Issue 5, pp 1024-1034.

World Meteorological Organization (WMO). 1994. *Guide to Hydrological Practices*. Fifth edition, WMO–No. 168, Geneva.

World Meteorological Organization (WMO). 1998. *Guide to Wave Analysis and Forecasting*. Second edition, WMO–No. 702, Geneva.

World Meteorological Organization (WMO). 2008. *Guide to Meteorological Instruments and Methods of Observation*. Seventh edition, WMO–No. 8, Geneva.

Yates, D.S., Moore, D.S. and Starnes, D.S. 2008. *The Practice of Statistics*, 3rd ed. Freeman. ISBN 978-0-7167-7309-2

Appendix 3.1: Internet links to reference documents and procedures

1. **Draft General Guidelines on Sampling and Surveys – United Nations Framework Convention on Climate Change, 2009**

https://cdm.unfccc.int/EB/047/eb47_repan27.pdf
2. **Proposed New Baseline and Monitoring Methodologies for Estimating GHG Emissions from the Bumbuna Hydroelectric Project, Sierra Leone, CDM-NM00121 – United Nations Framework Convention on Climate Change, 2007**

http://cdm.unfccc.int/methodologies/PAmethodologies/publicview.html?status=pending&meth_ref=NM0121-rev
3. **Forest Inventory and Analysis National Core Field Guide. Volume 1, Field Data Collection Procedures for Phase 2 Plots – United States Department of Agriculture, 2006**

http://fia.fs.fed.us/library/field-guides-methods-proc/docs/2006/core_ver_3-0_10_2005.pdf
4. **Sediment Sampling Guide for Dredging and Marine Engineering Projects in the St. Lawrence River. Volume 1, Planning Guidelines – Environment Canada, 2002**

www.slv2000.qc.ec.gc.ca/bibliotheque/centre_docum/phase3/guide_sediments/Guide_vol_1_a.pdf
5. **Sediment Sampling Guide for Dredging and Marine Engineering Projects in the St. Lawrence River. Volume 2, Field Operations Manual – Environment Canada, 2002**

www.slv2000.qc.ec.gc.ca/bibliotheque/centre_docum/phase3/guide_sediments/Guide_vol_2_a.pdf
6. **Good Practice Guidance for Land-Use, Land-Use Change and Forestry. International Panel on Climate Change (IPCC), 2003**

www.ipcc-nggip.iges.or.jp/public/gpplulucf/gpplulucf_contents.html
7. **2006 IPCC Guidelines for National Greenhouse Gas Inventories. International Panel on Climate Change (IPCC), 2006**

www.ipcc-nggip.iges.or.jp/public/2006gl/index.html

8. International Organization for Standardization, Guidance and Sampling Procedures

Water quality – Sampling – Part 4: Guidance on sampling from lakes, natural and man-made

ISO 5667-4:1987

Abstract: Presents detailed principles to be applied to the design of programmes, techniques and the handling and preservation of samples of water. The main objectives are measurements of quality characterisation, of quality control and for specific reasons. Microbiological examinations are not included.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=11767

Water quality – Sampling – Part 1: Guidance on the design of sampling programmes and sampling techniques

ISO 5667-1:2006

Abstract: 2006 sets out the general principles for, and provides guidance on, the design of sampling programmes and sampling techniques for all aspects of sampling of water (including waste waters, sludges, effluents and bottom deposits).

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=36693

Water quality – Guidance on analytical quality control for chemical and physicochemical water analysis

ISO/TS 13530:2009

Abstract: ISO/TS 13530:2009 is applicable to the chemical and physicochemical analysis of all types of waters. It is not intended for application to the analysis of sludges and sediments (although many of its general principles are applicable to such analysis) and it does not address the biological or microbiological examination of water. Whilst sampling is an important aspect, this is only briefly considered.

www.iso.org/iso/catalogue_detail.htm?csnumber=52910

Water quality – Sampling – Part 12: Guidance on sampling of bottom sediments

ISO 5667-12:1995

Abstract: Provides guidance on the sampling of sediments from rivers, streams, lakes and similar standing waters and estuaries. Sampling of industrial and sewage works' sludges and ocean sediments are excluded.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=11776

Water quality – Sampling – Part 14: Guidance on quality assurance of environmental water sampling and handling

ISO 5667-14:1998

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=24199

Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples

ISO/CD 5667-3

Abstract: ISO 5667-3:2003 gives general guidelines on the precautions to be taken to preserve and transport all water samples including those for biological analyses but not those intended for microbiological analysis.

These guidelines are particularly appropriate when spot or composite samples cannot be analysed on-site and have to be transported to a laboratory for analysis.

www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?csnumber=33486

Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams

ISO 5667-6:2005

Abstract: ISO 5667-6:2005 sets out the principles to be applied to the design of sampling programmes, sampling techniques and the handling of water samples from rivers and streams for physical and chemical assessment. It does not apply to the sampling of estuarine or coastal waters and has limited application to microbiological sampling.

It does not apply to the examination of sediment, suspended solids or biota.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=34815

Water quality – Evaluation of the aerobic biodegradability of organic compounds at low concentrations – Part 2: Continuous flow river model with attached biomass

ISO 14592-2:2002

Abstract: ISO 14592-2:2002 specifies a method for evaluating the biodegradability of organic test compounds by aerobic micro-organisms in natural waters by means of a continuous-flow river model with attached biomass.

ISO 14592-2:2002 applies to organic test compounds present in lower concentrations than those of natural carbon substrates also present in the system. Under these conditions, the test compounds serve as a secondary substrate and the kinetics for biodegradation would be

expected to be first order (non-growth kinetics).

ISO 14592-2:2002 applies to organic test compounds, which under the conditions of the test and at the chosen test concentration are water soluble; quantitatively detectable with appropriate analytical methods or available in radiolabelled form; non-volatile from aqueous solution; not significantly adsorbed; not photolyzed; and not inhibitory to the micro-organisms of the test system.

This test is not recommended for use as proof of ultimate biodegradability (mineralisation), which is better assessed using other standardised tests.

www.iso.org/iso/catalogue_detail.htm?csnumber=24871

Water quality – Evaluation of the aerobic biodegradability of organic compounds at low concentrations – Part 1: Shake-flask batch test with surface water or surface water/sediment

ISO 14592-1:2002

ISO 14592-1:2002 specifies a test method for evaluating the biodegradability of organic test compounds by aerobic microorganisms in surface waters by means of a shake-flask batch test with suspended biomass. It applies to natural surface water, free from coarse particles to simulate a pelagic environment (pelagic test); or to surface water with suspended solids or sediments added to obtain a level of 0.1 g/l to 1 g/l dry mass (suspended sediment test) to simulate a water-to-sediment interface or a water body with resuspended sediment material.

ISO 14592-1:2002 applies to organic test compounds present in lower concentrations (normally below 100 micrograms per litre) than those of natural carbon substrates also present in the system. Under these conditions, the test compounds serve as a secondary substrate and the kinetics for biodegradation would be expected to be first order (non-growth kinetics).

This test method is not recommended for use as proof of ultimate biodegradation, which is better assessed using other standardised tests. It does not apply to studies on metabolite formation and accumulation, which require higher test concentrations.

www.iso.org/iso/catalogue_detail.htm?csnumber=24870

Water quality – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium – Carbon dioxide evolution test

ISO 9439:1999

www.iso.org/iso/iso_catalogue/catalogue_ics/catalogue_detail_ics.htm?ics1=13&ics2=060&ics3=70&csnumber=26727

Water quality – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium – Method by analysis of inorganic carbon in sealed vessels (CO₂ headspace test)

ISO 14593:1999

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=24154

Water quality – Evaluation in an aqueous medium of the ‘ultimate’ aerobic biodegradability of organic compounds – Method by analysis of dissolved organic carbon (DOC)

ISO 7827:1994

Abstract: The conditions described do not always correspond to the optimal conditions allowing the occurrence of the maximum value of biodegradation. The procedure applies to substances which are soluble at the concentration used under the test conditions; non-volatile; not significantly adsorbable on glass; and not inhibitory to the test micro-organisms at the concentration chosen for the test.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=2219

Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide – Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test

ISO 14855-2:2007

Abstract: ISO 14855-2:2007 specifies a method for determining the ultimate aerobic biodegradability of plastic materials under controlled composting conditions by gravimetric measurement of the amount of carbon dioxide evolved. The method is designed to yield an optimum rate of biodegradation by adjusting the humidity, aeration and temperature of the composting vessel.

The method applies to the following materials:

- natural and/or synthetic polymers and copolymers, and mixtures of these;
- plastic materials that contain additives such as plasticisers or colourants;
- water-soluble polymers;

- materials that, under the test conditions, do not inhibit the activity of micro-organisms present in the inoculum.

www.iso.org/iso/catalogue_detail.htm?csnumber=40617

Water quality – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

ISO 8245:1999

www.iso.org/iso/catalogue_detail.htm?csnumber=29920

Water quality – Determination of ammonium nitrogen – Method by flow analysis (CFA and FIA) and spectrometric detection

ISO 11732:2005

Abstract: ISO 11732:2005 specifies methods suitable for the determination of ammonium nitrogen in various types of waters (such as ground, drinking, surface, and waste waters) in mass concentrations ranging from 0.1 mg/l to 10 mg/l (in the undiluted sample), applying either FIA or CFA. In particular cases, the range of application may be adapted by varying the operating conditions.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=38924

Water quality – Determination of nitrogen – Part 1: Method using oxidative digestion with peroxodisulfate

ISO 11905-1:1997

www.iso.org/iso/catalogue_detail.htm?csnumber=2155

Water quality – Determination of Kjeldahl nitrogen – Method after mineralisation with selenium

ISO 5663:1984

Specifies a procedure for the determination of trivalent negative nitrogen. Organic nitrogen in the form of azide, azine, azo, hydrazone, nitrite, nitro, nitroso, oxime or semicarbazone is not determined quantitatively. The procedure applies to the analysis of raw, potable and waste waters.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=11756

Water quality – Determination of selected organic nitrogen and phosphorus compounds – Gas chromatographic methods

ISO 10695:2000

www.iso.org/iso/catalogue_detail.htm?csnumber=18783

Water quality – Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection

ISO 13395:1996

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=21870

Water quality – Determination of nitrogen – Part 2: Determination of bound nitrogen, after combustion and oxidation to nitrogen dioxide, chemiluminescence detection

ISO/TR 11905-2:1997

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=23630

Water quality – Measurement of biochemical parameters – Spectrometric determination of the chlorophyll a concentration

ISO 23913:2006

Abstract: ISO 23913:2006 specifies flow injection analysis (FIA) and continuous flow analysis (CFA) methods for the determination of chromium(VI) in various types of water. The method applies to the following mass concentration ranges: for FIA (20 to 200 micrograms per litre and 200 to 2,000 micrograms per litre for surface water, leachates and waste water) and for CFA (2 to 20 micrograms per litre and 20 to 200 micrograms per litre for drinking water, ground water, surface water, leachates and waste water). The range of application may be changed by varying the operating conditions. Seawater may be analysed by these methods with changes in sensitivity and after adaptation of the reagent and calibration solutions to the salinity of the samples.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=37017

Water quality – Determination of pH

ISO 10523:1994

Abstract: The method specified (using a pH-meter) applies to all types of water and waste-water samples in the range from pH 3 to pH 10. The temperature, some gases and organic materials interfere with the pH-measurement. Suspended materials in the sample may cause significant errors. When measuring sewage and some surface waters, there is a particularly high risk of smearing the electrodes or contaminating the membranes and diaphragm with oil, grease or other contaminants.

www.iso.org/iso/catalogue_detail.htm?csnumber=18592

Water quality – Determination of electrical conductivity

ISO 7888:1985

Abstract: Specifies a method for the measurement of all types of water. The quantity can be used to monitor the quality of surface waters, process waters in water supply and treatment plants, and waste waters. Interferences are given.

www.iso.org/iso/catalogue_detail.htm?csnumber=14838

Water quality – Determination of turbidity

ISO 7027:1999

www.iso.org/iso/catalogue_detail.htm?csnumber=30123

Water quality – Determination of dissolved oxygen – Iodometric method

ISO 5813:1983

Abstract: Specifies the so-called Winkler procedure modified in order to make allowance for certain interferences. It is the reference procedure and applies to all types of water having concentrations greater than 0.2 mg/l, up to double saturation, which are free from interfering substances.

www.iso.org/iso/catalogue_detail.htm?csnumber=11959

Water quality – Determination of dissolved oxygen – Electrochemical probe method

ISO 5814:1990

Abstract: Includes a procedure by means of an electrochemical cell which is isolated from the sample by a gas permeable membrane. Depending on the type of probe employed measurement can be made either as concentration of oxygen, percentage saturation or both. The procedure is suitable for measurements made in the field and for continuous monitoring and in the laboratory. It is the preferred procedure for highly coloured and turbid waters. It is suitable for natural, waste and saline waters.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=11961

Water quality – Examination and determination of colour

ISO 7887:1994

Abstract: Cancels and replaces the first edition (1985). Specifies three methods for the examination of colour: a method for the examination of apparent colour by visually observing a water sample in a bottle; a method for the determination of the true colour of a water sample using optical apparatus; a method for the determination of the colour

by visual comparison with hexachloroplatinate standard solutions. Under certain circumstances, strongly coloured water samples need to be diluted before examination or determination.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=14837

Water quality – Determination of the chemical oxygen demand index (ST-COD) – Small-scale sealed-tube method

ISO 6060:1989

Abstract: Method specified is applicable to water with a value between 30 mg/l and 700 mg/l. The chloride contents must not exceed 1000 mg/l. If the value exceeds 700 mg/l, the water sample is diluted. For greatest accuracy it is preferable that the value of the sample is in the range of 300 mg/l to 600 mg/l.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=12260

Soil quality – Determination of soil microbial biomass – Part 1: Substrate-induced respiration method

ISO 14240-1:1997

Abstract: Contains a method for the determination of the active aerobic, heterotrophic microbial biomass in aerated agricultural and mineral soils.

www.iso.org/iso/catalogue_detail.htm?csnumber=21530

Soil quality – Determination of soil microbial biomass – Part 2: Fumigation-extraction method

ISO 14240-2:1997

Abstract: Gives a method for the determination of microbial biomass of soils by measurement of total extractable organic biomass material mainly from freshly killed microorganisms. It also applies to the estimation of microbial nitrogen and ninhydrin-reactive nitrogen in soil.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=23951

Soil quality – Sampling – Part 6: Guidance on the collection, handling and storage of soil under aerobic conditions for the assessment of microbiological processes, biomass and diversity in the laboratory suspensions

ISO 10381-6:2009

Abstract: ISO 10381-6:2009 provides guidance on the collection, handling and storage of soil for subsequent testing under aerobic conditions in the laboratory. The recommendations in this document are not applicable to the handling of soil where anaerobic conditions are to be maintained throughout.

ISO 10381-6:2009 applies mainly to temperate soils. Soils collected from extreme climates (e.g. permafrost, tropical soils) may require special handling.

www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=43691

Soil quality – Laboratory methods for determination of microbial soil respiration

ISO 16072:2002

Abstract: ISO 16072:2002 describes methods for the determination of soil microbial respiration of aerobic, unsaturated soils. The methods are suitable for the determination of O₂ uptake or CO₂ release, either after addition of a substrate (substrate-induced respiration), or without substrate addition (basal respiration).

ISO 16072:2002 applies to the measurement of soil respiration in order to:

- determine the microbial activity in soil (see [2]);
- establish the effect of additives (nutrients, pollutants, soil improvers, etc.) on the metabolic performance of microorganisms;
- determine the microbial biomass (see [3]);
- determine the metabolic quotient qCO₂.

www.iso.org/iso/catalogue_detail.htm?csnumber=32096

Soil quality – Determination of organic and total carbon after dry combustion (elementary analysis)

ISO 10694:1995

Abstract: Specifies a method for the determination of the total carbon content in soil after dry combustion. The organic carbon content is calculated from this content after correcting for carbonates present in the sample. If carbonates are removed beforehand, the organic carbon content is measured directly. Applies to all types of air-dried soil samples.

www.iso.org/iso/catalogue_detail.htm?csnumber=18782

Soil quality – Determination of organic carbon by sulfochromic oxidation

ISO 14235:1998

www.iso.org/iso/catalogue_detail.htm?csnumber=23140

Greenhouse gases – Part 2: Specification with guidance at the project level for quantification, monitoring and reporting of greenhouse gas emission reductions or removal enhancements

ISO 14064-2:2006

Abstract: ISO 14064-2:2006 specifies principles and requirements and provides guidance at the project level for quantification, monitoring and reporting of activities intended to cause greenhouse

gas (GHG) emission reductions or removal enhancements. It includes requirements for planning a GHG project, identifying and selecting GHG sources, sinks and reservoirs relevant to the project and baseline scenario, monitoring, quantifying, documenting and reporting GHG project performance and managing data quality. www.iso.org/iso/catalogue_detail?csnumber=38382

Appendix 3.2: Equipment cost estimates

Equipment	Average cost (USD)	Remarks/models and suppliers	Country and date of estimate
Water sampler	400-900	Acrylic, PVC, horizontal or vertical, Wildco	United States, 2009
Box corer	2,000	Eijkelkamp (55 x 500 mm)	Canada, 2006
Clear terrestrial chamber	500	See Figure 3.14-3.55 and Table 3.5	Canada, 2009
Dark terrestrial chamber	500	See Figure 3.16 and Table 3.6	Canada, 2009
Aquatic floating chamber	400	Aluminium	Canada, 2009
Eddy covariance system	55,000	Without tower; Campbell Scientific	Canada, 2009
Tower	25,000	Expect variable and high additional costs for anchoring/foundation and annual inspection	Canada, 2006
Tripod	2,000	Campbell Scientific	Canada, 2007
Funnel	400	Hardware stores	Canada, 2009
CO ₂ analyser	6,000	EGM-4 and Ciras-SC from PP Systems, Li-840 from LICOR Biosciences	United States, 2009
CH ₄ analyser	25,000	Picarro, Los gatos	United States, 2009
CH ₄ underwater sensor	9,000	METS, semiconductor underwater sensor, Franatech	Germany, 2008
Multiple gas analyser	55,000	Gasmet, Los Gatos	United States, 2009
Gas chromatograph	60,000	GC, 3 detectors (TCD, FID, ECD) and automated sampler	Canada, 2009

4. Calculation Manual

4.1 Introduction

4.2 Spatial extrapolation of gross GHG field data

4.3 Temporal integration

4.4 Adequacy analysis of the spatial and temporal resolution

4.5 Calculation of net emissions

4.6 Evaluation of uncertainties

4.7 Final presentation of results

4.8 References



4.1. Introduction

4.1.1. Objectives

The *Calculation Manual*'s objective is to provide guidance to standardize procedures on how to calculate net GHG emissions that arise from creating a reservoir in a river basin. The *Calculation Manual* is to be used mainly with measured and calculated GHG emission rates from field measurements, obtained as indicated at section 3 (*Field Manual*). This includes GHG emissions for carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O), and also carbon and nitrogen stocks, for terrestrial and aquatic ecosystems, under pre- and post-impoundment conditions.

This manual is meant to be living and dynamic, to be updated often.

According to UNESCO/IHA (2008, 2009), net GHG emissions are the difference between gross GHG emissions pre⁷- and post-impoundment, from the portion of the river basin influenced by the reservoir (both terrestrial and aquatic ecosystems) at the whole watershed level, including upstream and downstream. Also, to allow full life-cycle assessments (LCAs), emissions due to the above-water decay of flooded trees and other vegetation – and where the water table is elevated along the shoreline – have to be accounted for, as do emissions from the construction phase of the dam. The latter include the use of fossil fuels by machinery and the production of building materials such as concrete, steel, fuel, and others – even when they are not considered to be important for the reservoir's whole life cycle. As detailed LCA analyses are not the object of this manual, the use of standard procedures for LCA analysis of constructions are suggested, such as ISO 14040 (2006), Cooper and Fava (2006), Scientific Applications International Corporation/USEPA (2006), Hendrickson et al. (2005), Guinée (2002). Carbon stock change should also be assessed, including carbon buried in sediments.

4.1.2. Use of this Calculation Manual

As part of the UNESCO/IHA GHG Project, the present version of the *Calculation Manual* is

intended for use by qualified technicians and scientists to assess GHG emissions in a sample of representative sites worldwide. Future versions can introduce a tiered approach, allowing other uses. The *Calculation Manual* is to apply worldwide, for all types of climate and different reservoir and river-basin conditions, and for reservoirs of all types and purposes.

Again, as stated in previous sections, this manual is not meant as a general method for routine assessment and monitoring in existing and future reservoirs. Rather, it proposes standard procedures to make it easier to compare and transfer detailed field data collected from reservoirs and watersheds.

As input, the *Calculation Manual* uses the reservoir's hydrological, climatic, physical, chemical and biological characteristics (including drainage and flooded areas, topography, reservoir volume, reservoir operation, residence time and others) and estimates of GHG and emission rates from field measurements, obtained as indicated in the *Field Manual*.

Figure 1.1 (section 1) demonstrates the applicability of this *Calculation Manual*, within the context of the *Guidelines*.

4.2. Spatial extrapolation of gross GHG field data

The number of sampling stations depends on a compromise between budget, manpower and detailed objectives. The number of sampling points and the sampling frequency depend on the heterogeneity of the system and desired resolution.

A set of methods is presented in the section 3 (*Field Manual*) to determine the number and location of gauging stations, and the frequency and duration of the field measurements, including pre- and post-impoundment conditions. Each station will produce information applicable to an area of influence⁸ that the station is representing. Section 3 also describes how to obtain point estimates of gross GHG emission (or removal) rates per area unit for each station.

This section introduces guidance on how to extrapolate from the point samples estimates (obtained as described in the section 3) to areal

7 It is important to emphasise that the gross pre-impoundment emissions refers to the gross emissions that would occur in the same conditions before impoundment.

8 The definition of the areas of influence depends on the spatial distribution of the gauging stations, but also on the type of emission being measured. For example, diffusion is calculated for the whole reservoir area, while bubbling should only take into account the area where it is more likely (generally where the depth is between 0 to 10 m, although the bubbling area has often been observed to exceed the 10-metre depth zone), and degassing is a point measurement (at the generating station). For stratified sampling, each stratum can be associated to its total area.

units. It introduces standard procedures to estimate the mean or total values of the measured emissions in the system (and the associated variances), adopting the sample precision requirements as defined in the section 3. Finally, it presents guidance on how to integrate all the points to estimate the gross (total) GHG emissions from the whole area of interest, for pre- and post-impoundment conditions.

4.2.1. Sampling approaches

The choice of which type of sampling approach to propose depends on several considerations, including the types of information to be collected through sampling, the known characteristics of the population, and the cost of information gathering (UNFCCC, 2009). Some of the most common sampling methods are as follows:

- Simple random sampling – the most straightforward method for designing a sample;
- Systematic sampling – a statistical method involving the selection of elements from an ordered sampling frame;
- Stratified random sampling – the population is divided into relatively homogeneous subgroups, called strata, so that each different subpopulation (stratum) is sampled independently;
- Clustered sampling – a technique where the population is divided into sub-groups (clusters), and the sub-groups are sampled, rather than the individual elements to be studied;
- Multi-stage sampling – a complex form of cluster sampling, where the units (referred to as primary units) in the population are divided into smaller sub-units (referred to as secondary units), similar to cluster sampling;

All these sampling methods are summarized in section 3.2.2.1, with guidelines on circumstances where each is most applicable. For complete descriptions of these methods, see Annex 27 from the Clean Development Mechanism Executive Board, Meeting 47 (UNFCCC, 2009).

In the case of GHG emissions from freshwater reservoirs, stratified sampling should be preferred over other sampling approaches whenever possible (see section 3.2.1). For example, each of the different GHG fluxes (such as inflow to the reservoir, reservoir emissions, emissions

downstream of the dam) for each of the species of interest (CO_2 , CH_4 , N_2O) and each of the main pathways (water surface diffusion, bubbling and degassing), under a specific set of conditions (for example, land use, soil and vegetation type) can correspond to a different stratum. In this case, aquatic and terrestrial data could be treated separately, with the different strata being classified by land use (terrestrial) and type of aquatic environment (river, lake, wetland, standing water, running water, etc).

4.2.2. Formulas for performing the estimates

The estimates must be reliable in terms of how closely they are likely to fall around the true population value in repeated samples. The purpose of sampling is to obtain unbiased and reliable estimates of the mean or total values of key variables to use in the calculations of greenhouse gas emissions. All accepted probability sampling methods provide formulas for estimating the mean value from the sample and the precision of this estimate, i.e., the probability that it falls within a given range of the true population value, based on the variability of individual measurements in the sample (UNFCCC, 2009).

Once the sampling approach has been selected, estimates of the mean value can be got from the sample. These mean values can be adopted to compute the total rates, as well as to calculate a minimum sample size necessary to achieve a given level of precision. The *Field Manual* introduces procedures for defining the sample precision requirements (desired precision/expected variance and sample size) under different conditions of data availability.

The following items describe the formulas for performing the estimates relative to simple random sampling (the most straightforward method for designing a sample) and for stratified random sampling (the method suggested in the *Field Manual* as preferred over other sampling approaches, whenever possible). The formulas provided on these sections (equations 1 to 10) are based on the description provided by UNFCCC (2009), and also according to Hansen (1953), Cochran (1977), Groves (1989, 2004), Kish (1995) and Levy and Lemeshow (1999). The formulas for the other sampling approaches presented in section 4.2.1 of this *Calculation Manual* can be found in UNFCCC (2009).

4.2.2.1. Estimates performed under simple random sampling

Under simple random sampling, each case in the sample frame has an equal probability of being selected into the sample. The estimate of the mean value from the sample is given by the formula:

$$\bar{y} = \sum \frac{y_i}{n}$$

where y_i denotes the value of y (the measurable variable of interest) for observed value i , and n denotes the sample size.

The total GHG emission is obtained by the product of the mean emission rates by the associated area of influence (see item 2.3).

The variance of the sample is given by the formula:

$$S^2 = \frac{\sum (y_i - \bar{y})^2}{n-1}$$

The standard deviation of the sample (also called standard error), denoted by the symbol s , is simply its square root.

The standard error of the mean y , a measure of the dispersion of the estimate of the mean value from the sample around the true population mean, is:

$$S_{\bar{y}} = \frac{s}{\sqrt{n}} \sqrt{1 - n/N}$$

where N denotes the number of elements in the population, and assuming that these elements are labelled $i=1, \dots, N$.

If n is large enough, the data can be assumed to be normally distributed according to the central limit theorem (Rice, 1995). In such cases, the probability that y falls within a specified range of the population mean is given by:

$$Prob \left\{ \bar{Y} - t \frac{s}{\sqrt{n}} \sqrt{1 - n/N} \leq \bar{y} \leq \bar{Y} + t \frac{s}{\sqrt{n}} \sqrt{1 - n/N} \right\} = Prob(t)$$

where N denotes the population mean of y , and t is the normal deviate corresponding to $Prob(t)$, i.e., the percentage of the normal probability density that falls within t standard deviations of the mean.

The formula also provides the basis for specifying the size of a sample, given a target level of precision for the estimate of the mean value and a prior estimate of the variance in the variable of interest in the population.

The formula for the required minimum sample size (n_{min}) to estimate the mean value of a variable (y) within an interval (l_t) at a designated probability P can be approximated by:

$$n_{min} = \frac{t_{crit,p}^2 \times S_y^2}{l_t^2}$$

where $t_{crit,p}$ is the t value corresponding to P , and S_y^2 is the variance of y .

This is applicable to a sampling distribution of statistics (e.g. averages, variances) of random samples. Another approach for one sample, often lopsided, is that one sample of measured GHG emissions can be numerically expressed by the average, standard deviation, median, lower quartile, upper quartile, smallest emission and highest emission.

4.2.2.2. Estimates performed under stratified random sampling

Under stratified random sampling, the population is divided into relatively homogeneous subgroups, called strata, producing a gain in precision for a given sample size, if the cases in each stratum are more homogeneous than across strata.

The estimate of the mean from a stratified random sample is:

$$\bar{y}_{st} = \sum W_h \bar{y}_h$$

where

$W_h = \frac{N_h}{N}$ denotes the stratum weight

and

$\bar{y}_h = \frac{\sum N_h y_{hi}}{N_h}$ denotes the sample mean in stratum h

with:

N_h denoting the total number of units in the stratum h

y_{hi} denoting the value for the i^{th} unit in stratum h

The total GHG emission of each stratum is obtained by the product of the mean emission rates by the associated area of influence (see item 2.3).

The variance of the mean estimate is given by:

$$V(\bar{y}_{st}) = \sum W_h^2 \frac{S_h^2}{n_h} (1 - f_h)$$

where:

n_h is the number of units in the sample in stratum h

$f_h = \frac{n_h}{N_h}$ denotes the sampling fraction in the stratum

$S_h^2 = \frac{\sum^{N_h} (y_{hi} - \bar{y}_h)^2}{N_h - 1}$ denotes the true population

variance in the stratum h

$\bar{y}_h = \frac{\sum^{N_h} y_{hi}}{N_h}$ denotes the true population mean in stratum h

If a random sample is taken in each stratum, then an unbiased estimate of S_h^2 is:

$$S_h^2 = \frac{1}{(n_h - 1)} \sum^{n_h} (y_{hi} - \bar{y}_h)^2$$

This produces an unbiased estimate of the overall variance of the sample mean:

$$S^2(\bar{y}_{st}) = \frac{1}{N^2} \sum N_h (N_h - n_h) \frac{S_h^2}{n_h}$$

That formula can be used to calculate a sample size necessary to achieve a given level of precision in the same manner as described for a random sample. The calculation requires prior estimates of the variances in each stratum. Given those prior estimates, an optimal allocation of the total sample across strata (n_h) can be calculated, and then the resulting variance (and standard error) for the different total sample sizes can be computed. This procedure determines the sample necessary to achieve a specified level of precision and confidence.

The optimal allocation of a sample across strata depends on the relative variances in each stratum and the cost of data collection per sample point. The formula for the optimal allocation is:

$$\frac{n_h}{n} = \frac{W_h S_h / \sqrt{c_h}}{\sum (W_h S_h / \sqrt{c_h})}$$

where c_h is the cost per sample point in stratum h .

4.2.3. Estimating the gross GHG emissions from the whole area of interest

Each of the point samples can be associated to the area of influence (see section 2) that this

specific station is representing. Or, in the case of stratified sampling, stratum emissions are defined by the average of the stations on the stratum, and each stratum can be associated to its total area.

The product of the estimated GHG fluxes by the respective areas of influence represents the total GHG emission/removal rates. The total (gross) GHG emissions by sources and removals by sinks in the area affected by the construction of a reservoir can be got by summing all the estimated emission/removal rates from each of the measuring stations. The estimates of the mean value obtained from the sample, as described in section 4.4.2.2, can be adopted to compute the total rates. The average emission/removal GHG flux is obtained by dividing the total rates by the whole inundated area.

All important fluxes (inflow to the reservoir, reservoir emissions by water surface diffusion, bubbling and degassing, leakage from the reservoir downstream of the dam) for all gases of interest (CO_2 , CH_4 , N_2O) should be well identified and represented, as well as the areas where they are more likely to occur. It is very important to properly identify the areas of influence of each station or stratum; the adoption of wrong values for the areas of influence can seriously affect the final estimates, either overestimating or underestimating the total emission/removal rates. For example, bubbling rates should be applied only to areas prone to GHG emission by bubbling and not to the whole reservoir area.

The gross GHG emissions from the whole area of interest has to be estimated for both pre- and post-impoundment conditions, using data from the aquatic and terrestrial components.

In the case of pre-impoundment conditions, the estimate has to take into consideration terrestrial and aquatic environments from the contributing catchment and the future reservoir area, the area downstream of the reservoir site and the carbon stock. In the absence of pre-impoundment field data, literature information or measurements at reference sites (or both) may be adopted to estimate all relevant land- and water-use conditions. Take care to adopt a sufficiently precise time series to cover seasonal changes (see section 4.3).

For post-impoundment conditions, emissions from the contributing catchment area, in the reservoir, in the drawdown zone (that is a terrestrial zone during part of the year), and downstream of the reservoir site have to be estimated.

All these estimates of gross GHG emissions for pre- and post-impoundment conditions will serve as a basis for the calculation of net emissions, as presented in section 4.5.

4.3. Temporal integration

Depending on the age of the reservoir, the complexity of the site, and the available resources, a different frequency of measurements can be adopted for each site. Section 3.2.1 suggests adopting continuous measurements at a few measurement points, and visiting more points on a seasonal basis to determine spatial variability and to validate the continuous measurements. When this is not possible, and field surveys are the only option left, the sampling interval can be adjusted based on a cost-benefit analysis to obtain the best possible representation of the temporal variability (diurnal, seasonal and annual) and event-driven variability (such as interference of fronts, thermal inversion and others) of the variables of interest. Also, estimations should be performed for the contributing catchment and for the downstream river.

Each of these situations covers different conditions of temporal resolution for data collection. The next sections provide guidance to ensure results are compatible and comparable, which allows the temporal integration of the available data.

4.3.1. Inter-annual variability

Significant inter-annual variation has been observed in several reservoirs. So at least two years' observation is recommended for mature reservoirs, provided the years of observation do not differ significantly from a mean hydrologic year. Younger reservoirs need more frequent measurements during the first years of monitoring. Also, for new reservoirs, if high CO₂ gross emissions are observed, longer periods (one to five years or more, up to 10 years) may be needed to account for emission reduction over the reservoir's lifetime.

The adoption of the average of the total estimated annual values is recommended. When longer records are available, a time-series consistency analysis (including outliers' analysis) should be performed to ensure representative results.

Statistical analysis should be applied to determine whether monitoring results in successive years can be considered similar, for a pre-defined degree

of significance. If so, future monitoring can be less frequent. If not, annual monitoring should continue until a steady state is reached (see Figure 3.2).

For a young reservoir, a year-by-year analysis is needed to properly identify and represent the period of high initial GHG emissions and the emission reduction trend over the reservoir's lifetime. This analysis should also be performed for mature reservoirs, to verify the hypothesis that creating a reservoir has a diminishing effect on emissions over time.

4.3.2. Seasonal variability

The seasonal variation of the fluxes from the whole reservoir system (including contributing areas, the reservoir and the river downstream) must be studied to allow an accurate estimation of the emissions from a reservoir. Emissions may vary by more than one order of magnitude within a year because of the seasonal variations of humidity, organic carbon supply, age, thermal stratification, irregular convective mixing, depth, and reservoir operation.

As discussed in section 2.3.2, where seasonality is important, at least four measurement campaigns per year are needed (or two measurement programmes a year, under special circumstances, when no other alternative is possible), but key parameters and GHG fluxes are likely to need monitoring every month to cover seasonal variability and provide robust mass balance measurements.

According to the temporal resolution of the available data, total daily, monthly or seasonal emission rates should be computed as follows:

- When continuous data is available, daily totals should be computed.
- Monthly totals should be estimated from monthly field data.
- Seasonal rates should be obtained when only four (or two) measurement campaigns are available per year.

The total annual emission will be obtained by summing all the balances performed. To get a better understanding of the system dynamics of continuity and of seasonality, analysis should be performed for any of these cases.

4.3.3. Nychtemeral variations

Short-term dynamics of the GHG emissions can be important and it may be necessary to take into account semi-diurnal stratification processes to provide more accurate gas measures. Section 3.2.4 recommends at least one measurement during the day and one during the night in tropical reservoirs (especially during periods of reservoir stratification).

When semi-diurnal data (or continuous data) is available, the total daily emission will be estimated as the sum of the results from the analyses of the two different periods: emissions by day and night.

4.4. Adequacy analysis of the spatial and temporal resolution

A set of methods is presented in section 3.2 to determine the number and location of gauging stations, and the frequency and duration of the measurements, taking into account available budget, manpower and detailed objectives, either heuristically or using statistical tools to ensure a desired accuracy.

The need to refine the sampling plan based on the analysis of results is addressed in section 3.2.1. In this way, resolution must be an integral part of both planning and evaluation, using an adaptive measurement design (i.e., revising the resolution after analysing the initial data).

The present section aims to analyse the spatial and temporal adequacy of the available field data to determine net GHG calculation and also to re-evaluate the monitoring programme (as described by the feedback loop in Figure 1.1).

4.4.1. Internal adequacy analysis

The internal consistency analysis is performed to verify if the observed behaviour and trends are consistent when compared with other information from the area of interest (including pre- and post-impoundment conditions).

A statistical analysis of the data, including uncertainty analysis, allows comparison with the sample precision requirements as defined in the *Field Manual* (desired precision/expected variance). The procedures described in section 4.2.2 of this *Calculation Manual* can be adopted to obtain estimates of the mean value and variance

from the sample, as well as the precision of these estimates. These results allow verification if the original sample precision requirements are fulfilled, and, therefore, if the spatial and temporal resolution of the available data are adequate to achieve the desired level of precision. If this resolution is not adequate, it is necessary to make changes in the monitoring programme (see Figure 1.1 and sections 4.4.3 and 4.4.4).

The statistical analysis has to be complemented by an interpretation of the physical, chemical and biological data (including the hydraulics of the system), to improve understanding of the system behaviour. Any unexpected result has to be properly analysed to verify whether the observation is a true response of the system or a result of calculation, measurement or field planning errors – including insufficient space and time resolution, inadequate use of equipments, miscalculations, or other mistakes.

A comparison of the GHG emission data dynamics with some key parameter dynamics may allow identification of trends or relationships. These key parameters could be water quality parameters, terrestrial dynamics (such as seasonality in growth), hydrological (including water depth, rising or falling water, etc.) and meteorological (such as temperature, wind, pressure) variables, and also hydro operations for downstream emissions. A multiple regression analysis could be performed to evaluate the degree of correlation between the GHG emission data and the key parameters data. The relationships obtained have to be evaluated against theoretical knowledge and data from other studies (when available) to verify the general validity of the application (including use in other reservoirs).

4.4.2. Comparison to external references

Another way to evaluate the spatial and temporal adequacy of the available field data is by comparing the results to literature data, or by using reference water bodies and terrestrial systems, for both pre- and post-impoundment conditions.

The use of literature data comprises comparisons with other similar studies in aquatic environments, including other reservoirs as well as bodies of natural water. Any relevant contrasting result should be carefully examined, taking into consideration the similarities and differences between the studies.

The use of reference water bodies is also useful for analysing the field data, for pre- and post-impoundment conditions. Reference sites can provide information on the emissions under similar conditions to those of the reservoir and then give evidence to validate (or not) observations in the area of interest. Such sites can be used to identify normal variations due to climate or changes in land use, in both the aquatic and terrestrial ecosystems, and to ensure they are taken into account and not seen as reservoir effects.

If the comparison to external references cannot provide enough evidence to validate observed results, detailed analysis will be necessary to identify the reasons for any unusual behaviour.

4.4.3. Changes in pre-impoundment assessments

The results from the analyses performed according to items 4.4.1 and 4.4.2 may indicate that a new assessment of the pre-impoundment conditions is needed to confirm or invalidate observed results.

If the reservoir is still not inundated, new measuring campaigns can be performed, changing the spatial and temporal resolution of the field measurements (in both aquatic and terrestrial environments) to get a more appropriate representation of the pre-impoundment conditions.

If reference sites are used to assess pre-impoundment conditions, they have to be re-evaluated to see whether:

- the characteristics of the reference sites represent the pre-impoundment conditions;
- the spatial and temporal resolution of the measurements in the reference site are adequate.

In any of these scenarios, the search for literature data should be broadened to get the maximum possible information of the observed behaviour from other studies under similar conditions.

4.4.4. Changes in post-impoundment measuring design

The results from the analyses performed according to items 4.4.1 and 4.4.2 can indicate the need to change the spatial or temporal resolution of the field measurements (or both).

These changes can be necessary to increase or reduce the time and space definition. Adopting

the procedures described in section 4.2.2 enables the estimation of the new sample size needed to achieve the desired level of precision.

Another alternative is that the observed interrelationship between different measuring points and properties can allow a reduction in the measuring points, without significant loss of precision. As stated in the section 3.2.1 the results and analysis from an initial comprehensive survey can help to determine spots that are easily correlated to the observations on other measuring stations, and thus representative of a bigger area. In this case, the spatial resolution can be reduced, and field measurements (continuous or seasonal) may be taken at fewer representative sampling stations. The correlations would be used to estimate the emissions on the eliminated stations, based on the data observed on the representative sampling stations.

4.5. Calculation of net emissions

4.5.1. Main concept

Net GHG emissions are understood as the change in GHG emissions caused by the creation of a reservoir, over the whole affected area (including the reservoir and the drainage area, upstream and downstream of the dam). So, to quantify the net change of GHG exchange in a river basin caused by creating a reservoir, it is necessary to consider exchanges before, during and after its construction. In accordance with IPCC (2006), the lifecycle assessment period for net GHG emissions is 100 years. For the purpose of this document, net lifecycle GHG emissions are taken as a proxy for the reservoir's carbon footprint.

A good indication of the change in GHG emissions caused by creating a reservoir can be got by comparing pre- and post-impoundment conditions, and also taking into account the carbon load and dissolved GHG changes from the contributing drainage basin. Emissions from the construction phase are outside this document's scope, but can be estimated by the use of standard procedures for LCA analysis of constructions as suggested in section 4.1.1.

Take special care to correctly account for emissions attributable to natural and unrelated human sources. It is necessary to identify effects that are not induced by creating the reservoir and deduct the correspondent emissions from the computed totals.

4.5.2. Boundaries – direct and indirect impacts on emissions

Emissions related to modifications of the hydrology upstream of the reservoir and downstream of the dam have to be accounted for. Section 3.2.1 indicates how to define the limits for the analysis, including the contributing area upstream (and its input) and the affected area downstream.

In the case of pre-impoundment conditions, the calculation has to consider the catchment/reservoir terrestrial and aquatic environments, the area downstream of the reservoir site and also an assessment of carbon stock. In the case of post-impoundment conditions, emissions from the catchment, in the reservoir, and downstream of the reservoir site need to be taken into consideration. Downstream emissions comprise degassing and diffusive fluxes, and, according to Abril et al. (2005), their influence may range from a few tens of metres up to 50 km downstream in the river.

The influence of upstream reservoirs in a cascade reservoirs system has to be taken into consideration for both direct and indirect impacts on emissions. Direct impact on emissions is caused by outflow ('leakage') from the upstream reservoir that will be an inflow to downstream reservoirs. Take care to avoid double counting of emissions. Include indirect impacts on emissions in the analysis: water quality, carbon load and dissolved GHG changes from upstream reservoir can cause ecosystem changes in a downstream reservoir.

An important factor to remember is the analysis of other unrelated anthropogenic sources that may change, such as human settlements, industry, waste water, farming, and others. All these factors will directly influence the emissions, and cannot necessarily be attributed to the reservoir.

4.5.3. Carbon stock change

The evaluation of the carbon stock present in the area affected by the reservoir is critical in properly assessing the carbon budget. It is important to assess carbon mineralization in sediments, especially under anoxic conditions, to properly assess the amount of storage and carbon sequestration caused by the reservoir.

The carbon stock change can be an important part of the net GHG assessment if there is long-term burial of carbon in reservoir sediments. Therefore, it is necessary to estimate the total carbon stock, including components in the water and sediments.

GHG production after impoundment is related to the amount of decomposable carbon stock (including decomposable biomass in the reservoir and the carbon load from the watershed). Thus, the evaluation of the carbon stock present in the area to be flooded by the reservoir is a critical measurement, along with carbon loading from the catchment. The calculation should take into consideration the following:

- Biomass and soil organic carbon (SOC). Two types of biomass can be distinguished and both should be determined: the above-ground biomass (including living and dead biomass) and the below-ground biomass (roots). The SOC includes both living organisms and detritus and should also be quantified. Use maps of terrestrial habitats to quantify the biomass and SOC. Additional analyses on N, P and Fe could increase the level of information on such issues.
- Assessment of carbon transport in streams. Consider the particulate organic carbon (POC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) at representative stages of the hydrographs of the streams. When coupled with discharge calculations, this will permit determination of carbon transport.

4.5.4. Integrating the different results

4.5.4.1. Integrating emissions from the different gas species – CO₂, CH₄ and N₂O

Perform the emission calculations separately for each of the species in analysis (CO₂, CH₄ and N₂O) for pre- and post-impoundment conditions, obtained as described in section 4.2.3, and then transformed into CO_{2eq} (or, alternatively, C_{eq}) for computing total emission values and performing statistical analysis. Also present separately the results of the calculations for each of the three species as this allows comparison of their relative importance.

In the case of stratified sampling approach, calculate the emissions from each stratum independently, and then add them to compute the total GHG emission/removal rates for each of the species in analysis.

Global warming potential (GWP) as the conversion factor for calculation of gases' warming potential equivalences has to be used with care, as it is not widely accepted to correctly represent the relative weight of the gases on the change in global temperature.

4.5.4.2. Integrating the different pathways – diffusion, bubbling and degassing

Although the results from each of the three main pathways (diffusion, bubbling and degassing) should be presented separately, it is important to compute their total emission in the affected area.

Present all results as quantity/unit of time, but different conditions apply to each of the pathways:

- Calculate diffusion for the whole reservoir area.
- Only consider bubbling in the areas where it is more likely (generally where the depth is between 0 to 10 m, although several times the bubbling area has been seen to exceed the 10 metre depth zone).
- Degassing is a point measurement (at the generating station).

Hence, when converting diffusion and bubbling emissions into quantity/unit of time, multiply the estimated fluxes by the reservoir area (in the case of diffusion) or the affected area (for bubbling). This does not apply to degassing emissions, as they are not associated with any specific area of the reservoir.

4.5.4.3. Integrating the different areas – catchment, reservoir and downstream

Do not add or subtract from each other the results from the three emissions zones (contributing catchment, reservoir, downstream of the dam). They have to be presented separately to allow comparisons among them and with other study areas.

4.5.4.4. Integrating emissions, carbon fluxes and carbon stock

Emissions, carbon fluxes and carbon stock should not be integrated, but the results should be interpreted together to enable better understanding of the different processes involved. For example, carbon stock gives additional information to emission measurements and may explain the difference in emissions.

Carbon stock from the catchment, the reservoir and downstream from the reservoir can be integrated to get a general carbon balance in the reservoir:

$$\text{Carbon stock balance in the reservoir} = \text{stock inside reservoir} - \text{inputs} + \text{outputs}$$

Emissions and changes in carbon fluxes and stock should be considered over the life cycle of the reservoir. This means including changes in the carbon stock that would occur in the future even without the presence of the reservoir.

4.5.5. Upscale to 100 years

Calculate the study period of emissions for 100 years, as stated in section 4.5.1. Consider the reservoir's age to properly account for the initial increase and later decrease in emissions after impoundment, over the reservoir's lifetime.

Delmas et al. (2005) developed a model to assess GHG emissions throughout a reservoir's lifetime, in the form of an empirical expression for the time dependence of the average dissolved methane concentration in the Petit Saut reservoir over a 20-year period, based on three-and-a-half years of impoundment and data from the Buyo reservoir in Ivory Coast (Figure 4.1). A similar expression was calculated to describe the evolution of dissolved CO₂, based on the relationship between CH₄ and CO₂ concentrations, presented by Galy-Lacaux et al. (1999).

$$(\text{CH}_4)_t = [10.5 + 3.5 \cos(2\pi/12t)] e^{-0.015t}$$

$$(\text{CO}_2) = 6.11 (\text{CH}_4) + 22.5$$

where:

$(\text{CH}_4)_t$ is dissolved methane concentration in mg.L⁻¹;

t is the time in months;

(CO_2) is dissolved carbon dioxide concentration in mg.L⁻¹;

Note that these models are highly site-specific (or, at least, regionally specific). In the absence of a more general model that could be applied to the majority of reservoirs worldwide, it is possible to adopt the model proposed by Delmas et al. (2005) as a starting point for reservoirs in warm climates (this model, however, does not apply to boreal climates). Only directly use this relationship for reservoirs in which the CH₄ and CO₂ concentrations after the first months are very close to those in Figure 4.1. The equation, must be, at least, and in absence of other data, upscaled and adapted with the first results from measurements.

Similar models can be developed for other reservoirs. Important: under certain conditions, some reservoirs can contribute to carbon sequestration (see section 4.5.3 of this *Calculation Manual*), and this behaviour can also be included in the model.

4.5.6. Net GHG emissions – comparing pre- and post-impoundment conditions

The difference between pre- and post-reservoir gross GHG emissions/removals from the portion of the river basin influenced by the reservoir

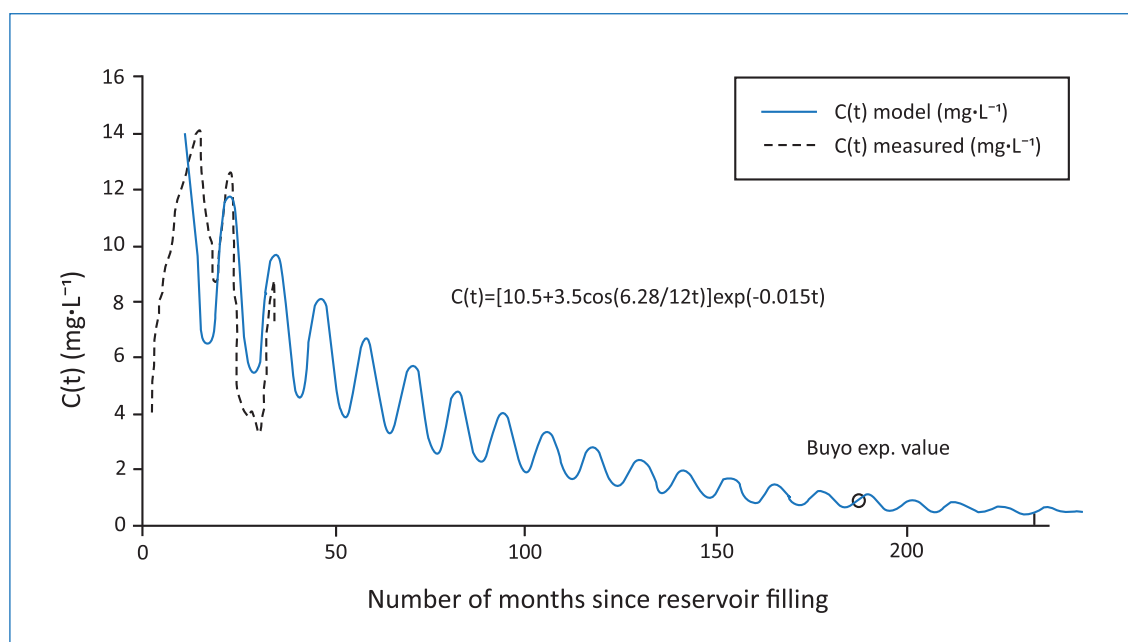


Figure 4.1: Modelled variations of dissolved CH₄ concentrations in the Petit Saut reservoir over a 20-year period based on the three first years of impoundment and data from an older reservoir with similar characteristics in the Ivory Coast (Buyo). Source: Delmas et al. (2005)

gives a good indication of the net GHG emissions/removals of the reservoir.

The estimates of gross emissions for pre- and post-impoundment conditions, obtained as described in section 4.2.3 and combined as indicated in section 4.5.4, can be adopted in calculating net GHG emissions.

To properly estimate the reservoir's carbon footprint over its whole lifetime, compare the total GHG emissions during the 100-year period of analysis with the pre-impoundment conditions.

Important: pre- and post-impoundment conditions refer only to the reservoir area. Regions outside the reservoir area could be used as a control or as an estimation of the pre-impoundment conditions if the true pre-impoundment conditions were not measured.

4.6. Evaluation of uncertainties

Reservoirs vary enormously in size and shape, and the processes controlling GHG emissions in these ecosystems vary considerably in space and time. These characteristics imply important uncertainties for the estimation of the change in GHG emissions caused by creating a reservoir.

Different forms of uncertainties can be identified:

- Natural, intrinsic or fundamental uncertainty – the uncertainty associated with the data, referring to natural variability.
- Technical or form uncertainty – the uncertainty associated with methods or techniques.
- Model uncertainty and error propagation – the uncertainty associated with modelling and upscaling procedures, including parameter value estimation.

The main issues to be considered in evaluating uncertainties affecting assessment of GHG emissions are as follows:

a. Quantifying variability

This is a key element in evaluating uncertainty. It can be done by parametric or non-parametric statistical methods to calculate variability (e.g. standard deviation, inter-quartile range). For the choice of statistics it is important to look at the data distribution and to choose the most appropriate statistical methods given the data. For example, non-normally distributed data require non-parametric statistics.

b. Transparency

Introduce clear and transparent (traceable) descriptions of variability/uncertainty calculations and motives behind various choices (e.g. statistical methods) to allow independent evaluation of uncertainties.

c. Natural, intrinsic or fundamental uncertainty

Natural uncertainty is the uncertainty associated with natural variability of the data. It can be estimated by taking a sample

that should be representative, consisting of replicate samples.

Uncertainty is reduced by increasing the number of replicate samples.

It is important to consider at what scale (temporal or spatial) and for what process the variability/uncertainty should be quantified. For example, ebullition is more variable than diffusive flux. Collecting system information can help in evaluating/understanding some of the variability (e.g. outliers).

d. Technical or form uncertainty – sampling and error analysis

The uncertainty related to methods can be estimated by repeated analysis of the same sample, by inter-calibration, or by comparison of different methods/techniques/protocols.

It is important to clarify specific conditions/details in the measurement protocol to minimize this uncertainty. Also it would be preferable to adopt a uniform protocol where procedures and sample treatments are specified and followed at all times.

e. Model uncertainty and error propagation

In models and extrapolations, numbers with different uncertainties are combined to produce new numbers. So it is important to calculate combined variability estimates when making such calculations or extrapolations. For example, the upscaling from flux per m² to flux for the whole reservoir requires consideration of both flux uncertainty and the uncertainty in the reservoir area estimate. Extrapolation exercises should take place early in the data collection process to identify possible problems with large uncertainty and adapt measurement procedures to reduce this uncertainty. For example, more replicates may be needed to account for error propagation at extrapolation.

A part of the method is also defining the models and deciding what processes to include. To account for uncertainty caused by such choices, compare the approaches in various models. Uncertainty over models can be evaluated by simple regression coefficients, validation procedures (e.g. difference between predicted versus observed), and sensitivity analyses.

Important: the behaviour of models that are not purely physical models (grey- or black-box models) cannot be validated for conditions other than the ones used to define and

calibrate them. This limits the use of these models for forecasting outside the conditions for which they were defined/calibrated.

For a detailed description of all these elements, see the *IPCC Good Practice Guidance and Uncertainty management in National Greenhouse Gas Inventories – Annex 1: Conceptual Basis for Uncertainty Analysis (IPCC, 2000)*.

4.7. Final presentation of results

This section summarizes how the results have to be presented, including the variables to be included and the units to be adopted.

4.7.1. Emissions from the different gas species – CO₂, CH₄ and N₂O

Present separately the emission for each of the species in analysis (CO₂, CH₄ and N₂O), for pre- and post-impoundment conditions, in grams of GHG per m² per day (g x m⁻²d⁻¹), and also transform them to CO_{2eq} or C_{eq}.

Also present total emissions, obtained from the addition of the values obtained in CO_{2eq} or C_{eq}.

Clearly state the conversion factor for calculating CO_{2eq} or C_{eq}.

4.7.2. Emissions from the different pathways – diffusion, bubbling and degassing

Present separately the results from each of the three main pathways (diffusion, bubbling and degassing), for pre- and post-impoundment conditions, in CO_{2eq} or C_{eq}.

Also state the total emission resultant in the affected area, obtained from the addition of the values obtained in CO_{2eq} or C_{eq}.

Also give the areas of influence from all pathways (in m² or in km²), as well as the total areas.

4.7.3. Emissions from the different areas – catchment, reservoir and downstream

Do not add or subtract from each other the results from the different emissions zones (including contributing catchment, reservoir, and downstream of the dam). Present them separately, for pre- and post-impoundment conditions, using the same units defined in sections 4.7.1 and 4.7.2, to allow comparisons among them and with other study areas.

4.7.4. Carbon stock

Present results for the carbon stock from the contributing catchment, the reservoir and downstream of the dam from the reservoir for pre- and post-impoundment conditions including, whenever possible:

- TOC – total organic carbon (mg/L);
- DOC – dissolved organic carbon (mg/L);
- DIC – dissolved inorganic carbon (mg/L);

- POC – particulate organic carbon (mg/L).

Consider emissions and changes in carbon fluxes and stock over the reservoir’s life cycle.

4.7.5. Measurement Questionnaire

When applicable, also present characteristics of the reservoir, ancillary parameters, summary of the equipment, quantity and frequency of the measurements, as specified in the Measurement Questionnaire (Appendix 4.1).

4.8. References

- Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Santos, M. A., and Matvienko, B. 2005. Carbon dioxide and methane emissions and the carbon budget of a 10-years old tropical reservoir (Petit-Saut, French Guiana). *Global Biogeochem. Cycles* 19: GB 4007, doi:10.1029/2005GB002457.
- Cochran, W.G. 1977, *Sampling Techniques*, 3rd edn, Wiley, New York.
- Cooper, J.S.; Fava, J. 2006. Life Cycle Assessment Practitioner Survey: Summary of Results, *Journal of Industrial Ecology*
- Delmas, R., Richard, S., Guérin, F., Abril, G., Galy-Lacaux, C., Grégoire, A. 2005. Long-term greenhouse gas emissions from the hydroelectric reservoir of Petit Saut (French Guiana) and potential impacts. In pages 293–312. In Tremblay, A., L. Varfalvy, C. Roehm and M. Garneau (eds.). *Greenhouse Gas Emissions: Fluxes and Processes, Hydroelectric Reservoirs and Natural Environments*. Environmental Science Series, Springer, New York.
- Galy-Lacaux, C., Delmas, R., Jambert, C., Kouadio, G., Richard, S., Gosse P. 1999. Long-term greenhouse gas emissions from hydroelectric reservoirs in tropical forest regions. *Glob Biogeochem Cycles* 13: 503–517.
- Groves, R.M. 1989, *Survey errors and survey costs*, Wiley, New York.
- Groves, R.M. 2004, *Survey methodology*, J. Wiley, Hoboken, NJ.
- Guinée, J. ed. 2002. *Handbook on Life Cycle Assessment: Operational Guide to the ISO Standards*, Kluwer Academic Publishers.
- Hansen, M.H. 1953, *Sample survey methods and theory*, Wiley, New York.
- Hendrickson, C. T., Lave, L. B., and Matthews, H. S. 2005. *Environmental Life Cycle Assessment of Goods and Services: An Input-Output Approach*, Resources for the Future Press.
- Intergovernmental Panel on Climate Change (IPCC). 2000. *IPCC Good Practice Guidance and Uncertainty management in National Greenhouse Gas Inventories*. Prepared by the National Greenhouse Gas Inventories Programme. Published: IGES, Japan.
- Intergovernmental Panel on Climate Change (IPCC). 2006. *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. Prepared by the National Greenhouse Gas Inventories Programme. Edited by H.S. Eggleston, L. Buendia, K. Miwa, T. Ngara and K. Tanabe. Published: IGES, Japan.
- ISO 14040. 2006. *Environmental management – Life cycle assessment – Principles and framework*, International Organisation for Standardisation (ISO), Geneva.
- Kish, L. 1995, *Survey sampling*, Wiley classics library edn, Wiley, New York.
- Levy, P. and Lemeshow, S. 1999, *Sampling of populations: methods and applications*, Wiley, New York.
- Rice, . (1995), *Mathematical Statistics and Data Analysis* (Second ed.), Duxbury Press, ISBN 0-534-20934-3.
- Scientific Applications International Corporation / USEPA. 2006. *Life cycle assessment: principles and practice*, pp. 88, www.epa.gov/NRMRL/lcaccess/pdfs/600r06060.pdf
- UNESCO/IHA. 2008. *Assessment of the GHG status of freshwater reservoirs: scoping paper*. Working Group on Greenhouse Gas Status of Freshwater Reservoirs. International Hydrological Programme. 28p. IHP/GHG-WG/3.
- UNESCO/IHA. 2009. *The UNESCO/IHA Measurement Specification Guidance for Evaluating the GHG Status of Man-Made Freshwater Reservoirs*. Edition 1 – June 2009
- United Nations Framework Convention on Climate Change (UNFCCC). 2009. *Draft general guidelines on sampling and surveys*. EB 47 report, annex 27, CDM – Executive Board. 28 May 2009.

Appendix 4.1 – Measurement questionnaire

In collaboration with UNESCO, IHA is working on a Greenhouse Gas (GHG) Research Project, which aims to improve understanding of the effect of reservoirs on natural GHG emissions. Currently, the project's main activity is to apply the measurement specification *Guidelines* to a representative set of reservoirs.

Section 1

This section identifies your reservoir and helps us to understand the findings in their climatic and regional context and make the data comparable.

Reservoir:

Name:	
Country:	
Location (x°N/y°E):	
Altitude:	
River/basin:	
Start of construction:	
End of construction:	
Commissioning date:	
Impoundment date:	
Type of flooded vegetation:	

☐ Hydropower

☐ Water supply

☐ Recreation

☐ Irrigation

☐ Flood management

☐ Settling pond

☐ other (specify):

From the list below, please choose the climatic zone that best describes the region of your reservoir (list according to Köppen-Geiger climate classification):

☐ Tropical rain forest climate (Af)

☐ Maritime temperate climate/oceanic climate (Cfb)

☐ Tropical monsoon climate (Am)

☐ Maritime subarctic climate/subpolar oceanic climate (Cf)

☐ Tropical wet and dry or savannah climate (Aw)

☐ Hot summer continental climate (Dfa, Dwa, Dsa)

☐ Dry arid climate (Bw)

☐ Warm summer continental climate (Dfb, Dwb, Dsb)

☐ Semiarid climate (Bs)

☐ Continental subarctic or boreal climate (Dfc, Dwc, Dsc)

☐ Mediterranean climate (Cs)

☐ Continental subarctic climate with severe winters (Dfd, Dwd)

☐ Humid subtropical climate (Cfa Cwa)

☐ Polar climate (Et)

Length of the ice-free period (days):

Topobathymetric information

Section 1

This section identifies your reservoir and helps us to understand the findings in their climatic and regional context and make the data comparable.

Drainage area (km ²):	
Flooded area (km ²):	Min:
	Max:
	River bed:
Total flooded area:	
Aquatic flooded area:	
Reservoir volume (m ³ x10 ⁶):	Min:
	Max:
Shoreline length (km):	

Depth (m):	Annual	Season	
		wet	dry
Mean			
Max			

Section 2

This section identifies which parameters were measured in the reservoirs and it helps us to generalize observations from different regions.

Have you measured any of the following parameters in the reservoir?

	frequency of measurements per year	Min	Max	Mean	N
Mean annual rainfall (mm)					
Mean long-term incoming flow (m ³ /s)					
Mean wind speed (m/s)					
Residence time (in days)					
Current speeds in rivers and streams (m/s)					
Wave height (m)					
Concentrations of organic matter (mg/L)					
Concentrations of nitrogen (mg/L)					
Concentration of phosphorus (mg/L)					
Concentration of iron (mg/L)					
Supply nutrients (mg/L)					

Section 2

This section identifies which parameters were measured in the reservoirs and it helps us to generalize observations from different regions.

Have you measured any of the following parameters in the reservoir?

	frequency of measurements per year	Min	Max	Mean	N
Biomass of plants, algae, bacteria and animals in the reservoir (t/ha)					
Biomass of plants, algae, bacteria and animals in the drawdown zone (t/ha)					
Water temperature (°C)					
Turbidity (NTU – nephelometric turbidity units)					
Total alkalinity (mg $\text{C}_3\text{CO}_3/\text{L}$)					
Conductivity (mS/cm)					
pH value					
pCO ₂ (ppm)					
pCH ₄ (ppm)					
pN ₂ O (ppm)					
Carbon in sediments (%)					
DO – Dissolved oxygen (mg/L)					
BOD – Biochemical oxygen demand (mg/L)					
COD – Chemical oxygen demand (mg/L)					
TOC – Total organic carbon (mg/L)					
DOC – Dissolved organic carbon (mg/L)					
DIC – Dissolved inorganic carbon (mg/L)					
POC – Particulate organic carbon (mg/L)					
Water transparency (m)					
Water colour					
other (specify)					

Please describe the characteristics of the reservoir with regard to the following components.
Stratification
Stability of density stratification in the water
Sediment load
Reductions in hydrostatic pressure as water is released through reservoir outlets
Increased turbulence downstream of the dam with ancillary structures e.g. weirs
Depth of the water intake

Section 3

This section summarizes the findings. Please specify the equipment you used, the frequency of emissions that were measured and the quantities you were able to identify.

Which of the following did you measure?

☐ Pre-impoundment

☐ Post-impoundment

☐ Terrestrial

☐ Aquatic

☐ Upstream

☐ Downstream

☐ Diffusive fluxes (specify method and gas analyzer)

☐ Degassing (specify method and gas analyzer)

☐ Bubbling (specify method and gas analyzer)

If you measured the pre-impoundment emissions at reference sites, please indicate their name, location and type (lake, river, other):

When (hour, day, month, year, during ice-free period and under ice) were measurements taken in your reservoir and why?

How measurements were performed? If using a boat or hydroplane, were you anchored or drifting with the current (details of the method)?

Which terrestrial measurement systems did you use?

☐ Incubator

☐ Eddy covariance tower

☐ Chambers

☐ other (specify)

Section 3

This section summarizes the findings. Please specify the equipment you used, the frequency of emissions that were measured and the quantities you were able to identify.

Which aquatic measurement systems did you use?

- ☐ Surface floating chamber
- ☐ Thin boundary layer
- ☐ Bubbling
- ☐ other (specify)

Why did you use the chosen equipment? Please specify advantages and disadvantages for your reservoir:

Gross measurements of greenhouse gases (Grams of GHG per m ² per day (g x m ⁻² d ⁻¹)):	frequency of measurements per year	Replicate measurement	Min	Max	Mean	n
Carbon dioxide (CO ₂)						
Methane (CH ₄)						
Nitrous oxide (N ₂ O)						
Other (specify)						

Solids in water (mg/L):	frequency of measurements per year	Replicate measurement	Min	Max	Mean	n
Total solids						
Suspended solids						
Dissolved solids						
Other (specify)						

Contact details of the measuring institution/department of company:

	Start of measurements:	
	End of measurements:	
	Budget in national currency:	
	Budget in USD:	

Thank you for taking the time to fill in this questionnaire.

5. Glossary

Bibliography



5. Glossary

The glossary defines some specific terms as the document authors intend them to be interpreted in these Guidelines.

Acidity

Having a *pH* value below 7.

Aerobic

Describes conditions or processes in water or sediments in which oxygen is present, as when CH_4 oxidises to CO_2 .

Algae

Simple rootless photosynthetic plants that grow in sunlit waters in relative proportion to the amounts of nutrients available. They can reduce the quality of water by lessening its *dissolved oxygen*.

Alkalinity

Having a *pH* value above 7.

Altimetry

The measurement of altitude of an object or a landscape above a fixed level.

Anaerobic

1. A life or process that occurs in, or is not destroyed by, the absence of oxygen.
2. A condition in which 'free' (atmospheric) or dissolved oxygen is NOT present in water.

Annual budget (of GHG emissions)

The balance of *GHG emissions* of a reservoir throughout the year. In most settings, GHG emissions vary considerably throughout the year; to adequately estimate the *net GHG emissions* of a given water body, the net emissions are then calculated over 12 months. It is recommended that the annual emission budget or, to achieve even greater precision if measurements are available, a several-year emission budget, is considered.

Anoxic

1. Denotes the absence of oxygen, as in a body of water.
2. Of, relating to, or affected with anoxia; greatly deficient in oxygen; oxygenless as with water.

Anthropogenic

Resulting from or produced by human beings.

Aquatic ecosystem (see Ecosystem)

Basin

The entire geographical area drained by a river and its tributaries, in which all surface run-off flows,

through a network of streams and rivers, to the same outlet.

Bathymetry

The measurement of depths and seabed contours of water bodies.

Benthic chamber (see Chamber)

Benthic flux

Discharge of gaseous substances from the ecological region at the lowest level of a water body, including the sediment surface and some sub-surface layers.

Biochemical oxygen demand (BOD)

The amount of *dissolved oxygen* consumed by micro-organisms (bacteria) in the bio-chemical oxidation of inorganic and *organic matter* in water.

Biomass

The total mass of living organisms in a given area, volume or ecosystem at a given time; recently-dead plant material is included as dead biomass. The quantity of biomass can be expressed either as a dry weight or by its energy, carbon or nitrogen content.

Biome

A major and distinct regional element of the biosphere, typically consisting of several *ecosystems* (e.g. forests, rivers, ponds, swamps) in a region. Biomes are characterized by typical communities of plants and animals.

Boreal climate (see also Climate)

Continental *climate* with long, very cold winters (up to six months with mean temperatures below freezing), and short, cool summers (50 to 100 frost-free days). Precipitation increases during summer months, although annual precipitation is still small.

Soil box corer

An instrument used to collect soil or sediment samples.

Bubbling (syn. Ebullition)

Discharge in the form of bubbles of gaseous substances from a water body, which results from carbonation, evaporation or fermentation.

Catchment (see Basin)

Carbon budget

The balance of the exchanges (incomes and losses) of carbon between the carbon reservoirs or between one specific loop (e.g., atmosphere ↔ biosphere) of the carbon cycle. An examination of the carbon budget of a pool or reservoir can provide

information about whether the pool or reservoir is working as a source or sink for carbon dioxide.

Carbon cycle

The biogeochemical cycle by which carbon is exchanged among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere of the Earth. It is one of the most important cycles of the Earth and allows for carbon to be recycled and reused throughout the biosphere and all its organisms.

The cycle is usually thought of as four major reservoirs of carbon interconnected by pathways of exchange. The reservoirs are the atmosphere; the terrestrial biosphere (which usually includes freshwater systems and non-living organic material, such as soil carbon); the oceans (which includes dissolved inorganic carbon and living and non-living marine biota); and the sediments (which includes fossil fuels). The annual movements of carbon, the carbon exchanges between reservoirs, occur because of various chemical, physical, geological, and biological processes. The ocean contains the largest active pool of carbon near the surface of the Earth, but the deep-ocean part of this pool does not rapidly exchange with the atmosphere.

Carbon dioxide (CO₂)

Carbon dioxide (chemical formula CO₂) is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It is a gas at standard temperature and pressure and exists in the Earth's atmosphere in this state. It is a naturally occurring greenhouse gas (GHG) fixed by photosynthesis into organic matter (OM). Carbon dioxide is used by plants during photosynthesis to make sugars, which may be consumed in respiration or used as the raw material to produce other organic compounds needed for plant growth and development. It is emitted during respiration by plants, and by all animals, fungi and microorganisms that depend directly or indirectly on plants for food. It is thus a major component of the carbon cycle. Carbon dioxide is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Amounts of carbon dioxide are emitted from volcanoes and other geothermal processes, such as hot springs and geysers, and by the dissolution of carbonates in crustal rocks.

Carbon dioxide equivalent emission

The amount of CO₂ emissions that would have the same *global warming potential (GWP)*, over

a given time horizon, as an emitted amount of a GHG or a mixture of GHGs. The CO₂-equivalent emission is obtained by multiplying the emissions of a GHG by its GWP for the given time horizon. For a mix of GHGs it is obtained by summing the CO₂-equivalent emission of each gas.

Carbon footprint

The total amount of carbon dioxide and other greenhouse gases emitted over the full life cycle of a product or service. It is usually expressed as grams of equivalents, which accounts for the different global warming effects of different greenhouse gases (Parliamentary Office of Science and Technology POST, 2006).

Carbon mass flow

The movement of mass (of carbon) from one location to another. Carbon in a water body can be in particulate or dissolved form and it can be organic and inorganic. The forms to be measured are:

- Total Organic Carbon (TOC),
- Dissolved Organic Carbon (DOC),
- Dissolved Inorganic Carbon (DIC),
- Particulate Organic Carbon (POC).

Carbon inputs and outputs to be considered are:

- carbon brought in by *macrophytes*,
- carbon exchanges with groundwater,
- carbon lost permanently to sediment,
- carbon exchanged with the atmosphere in the form of CO₂ and CH₄,
- humic substance income and output.

Carbon sequestration

Long-term storage of carbon dioxide or other forms of carbon to mitigate global warming. It can occur through a build-up of GHG concentration in vegetation, water or sediments. It determines the ability of a water body to act as a carbon sink. The uptake in sediments may be important if, without storage, these sediments would have been transported downstream, since they can provide *anoxic* conditions leading to CH₄ production in the reservoir.

Carbon sink

A natural or artificial reservoir that accumulates and stores some carbon-containing chemical compound for an indefinite period.

Carbon stock

The quantity of carbon contained in a 'pool',

meaning a reservoir or system that has the capacity to accumulate or release carbon.

Carbon storage (see *Uptake*)

CH₄ (see *Methane*)

Chamber (Floating chamber; Benthic chamber)

A terrestrial and aquatic GHG flux measurement tool, which can be static or dynamic, dark or transparent, and obtains measurements by calculating the increase of GHG concentration in the chamber over a time period or from samples taken at regular intervals and analysed by *gas chromatography*. Benthic chambers are used to measure *benthic fluxes* from sediments at the bottom of a water body. Floating chambers are used to measure *diffusive fluxes* at the air-water interface. Chambers are also used to measure *fluxes through macrophytes* at the air-water interface and GHG fluxes from vegetation.

Chemical oxygen demand (COD)

The amount of *dissolved oxygen* consumed by the chemical *decomposition* of organic or inorganic matter.

Climate

Climate in a narrow sense is usually defined as the average weather, or more rigorously, as the statistical description in terms of the mean and variability of 'relevant quantities' over a period of time ranging from months to thousands or millions of years. The relevant quantities are usually surface variables such as temperature, precipitation, and wind. The classical period for averaging these variables is 30 years, as defined by the World Meteorological Organisation.

CO₂ (see *Carbon dioxide*)

Conductivity

Measures the ability of a material to transmit electricity, heat, water or sound. The measurement unit is (mS/cm).

Convection (thermal)

Vertical transfer of heat through a fluid, usually caused by near-surface cooling or warming of water bodies.

Convective mixing (irregular)

Vertical mixing of fluxes and molecules in a water body due to the occurrence of thermal convection.

Covariance tower (see *Eddy covariance tower*)

Decomposition (of organic matter)

Chemical processes by which *organic matter* (OM) in a water body is transformed into gaseous end products. Major processes are

oxidative decomposition, *methanogenesis* and *de-nitrification*. Their respective end products are CO₂, CH₄ and N₂O.

Degassing

Degassing is defined as an emission that happens on discharge from low-level outlets, including turbine tailwater (induced by dramatic pressure change). A wide variation in the importance attributed to degassing has been reported (1% to 90% of total emissions), and it is influenced by dam design. Degassing downstream of a dam and spillway can be estimated by the difference between the gas concentration upstream (or in the turbine) and downstream of the power plant, multiplied by the outlet discharge. Among the main greenhouse gases, methane (CH₄) is more susceptible to be degassed compared to carbon dioxide (CO₂) and nitrous oxide (N₂O), because it is less soluble. However, all three gases should be monitored for degassing.

De-nitrification (see *Nitrification*)

Detritus

The remains of substances that have been destroyed or broken up.

Diffusive flux

Discharge of GHG from the air-water interface of a water body.

Dissolved inorganic carbon (DIC) (see *Carbon mass flow*)

Dissolved organic carbon (DOC) (see *Carbon mass flow*)

Dissolved oxygen (DO)

A relative measure of the amount of oxygen that is dissolved or carried in a given medium. It can be measured with a dissolved-oxygen probe such as an oxygen sensor or an optode in liquid media, usually water. The oxygen in a water body is often in its dissolved form. Its presence influences OM *decomposition* processes and provides oxygen for fish and other aquatic organisms' respiration. The measurement unit is mg/L.

Drainage area

The geographical area drained by a river and its tributaries.

Ebullition (see *Bubbling*)

Ecosystem (terrestrial and aquatic)

The interactive system formed from all living organisms and their abiotic (physical and chemical) environment in a given area. The boundaries of what could be called an ecosystem are somewhat

arbitrary, depending on the focus of interest or study. This Guidance distinguishes between aquatic and terrestrial ecosystems.

Eddy covariance tower

An atmospheric flux measurement instrument to measure and calculate vertical turbulent fluxes in atmospheric boundary layers. It statistically analyses high-frequency wind and scalar atmospheric data, and yields values of fluxes of these properties.

Emissions (see *GHG emissions*)

Epilimnion

The dense topmost layer of water in a thermally stratified water body.

Euphotic

The top layer of a water body that receives enough sunlight to allow for *photosynthesis*.

Eutrophic

Water with a high nutrient content (naturally or caused by pollution), resulting in high primary productivity of biomass.

Floating chamber (see *Chamber*)

Flooded area

The land area flooded during the impoundment of a reservoir. Seasonal changes mean its size can vary throughout the year, and *GHG emissions* in the drawdown zone may occur if vegetation re-grows when water levels are low. So it is recommended to measure both the minimum and the maximum flooded area (in km²).

Flux through macrophytes

Discharge of *GHG* at the air-water interface through plant stems and vegetation in water.

Gas chromatographer

A chemical analysis instrument used in analytic chemistry for separating and analysing compounds that can be vaporized without decomposition.

Geographic information system (GIS)

System, tool or software that allows for storage and analysis of spatial information and the editing of data and maps.

GHG (see *Greenhouse gas*)

GHG status of a reservoir

The change in GHG emissions in a river basin resulting from the creation of a freshwater reservoir (also known as the net GHG emissions). Net GHG emissions are the difference between gross GHG emissions pre- and post-impoundment, from the portion of the river basin influenced

by the reservoir (both terrestrial and aquatic ecosystems) at the whole watershed level, including upstream and downstream. Also, to allow full life-cycle assessments (LCAs), emissions have to be accounted for from:

- the dam's construction phase;
- the above-water decay of flooded trees and other vegetation;
- the elevation of the water table along the shoreline.

Global warming potential (GWP)

An index, based on the radiative properties of *GHGs*, measuring the radiative forcing of a unit mass of a given GHG in today's atmosphere integrated over a chosen time horizon, relative to that of CO₂. The GWP represents the combined effect of the differing lengths of time that these gases remain in the atmosphere and their relative effectiveness in absorbing outgoing infrared radiation. The IPCC considers the GWP of GHGs in a 100-year time frame. This conversion factor for calculating gases' warming potential equivalences has to be used with care, as it is not widely accepted to correctly represent the relative weight of the gases on the change in global temperature.

Greenhouse gas (GHG)

GHGs are the gaseous constituents of the atmosphere that absorb and emit radiation at specific wavelengths in the spectrum of thermal infrared radiation emitted by the Earth's surface, from the atmosphere itself, and through clouds. In this Guidance, the evaluation of *net emissions* from water bodies includes the three GHG species CO₂, CH₄, and N₂O.

Gross GHG emissions

Total *GHG emissions* measured at a reservoir's air-water surface. This is not representative of the reservoir's *GHG footprint*, since *net emissions* need to be considered.

Heterotrophic CO₂ respiration

Process where organisms other than plants convert organic matter (*OM*) to carbon dioxide (CO₂) through consumption.

Hydrologic cycle (syn. Water cycle)

Describes the succession of stages through which water passes from the atmosphere to the earth and its return to the atmosphere: evaporation, evapotranspiration, condensation, precipitation, interception, infiltration, percolation, runoff and storage in groundwater and water bodies.

Hydrology

Science that deals with the water in the earth: occurrence, circulation, distribution, quantification, and anthropic interactions. It includes the study of the movement, distribution, and quality of water throughout the Earth, including the hydrologic cycle and water resources.

Hydrostatic pressure

The pressure exerted by a fluid at equilibrium due to the force of gravity.

Hypolimnion

The dense bottom layer of water in a thermally stratified water body.

Infrared gas analyser (IRGA)

An instrument used to measure trace gases by determining the absorption of an emitted infrared light source through a certain air sample.

International System of Units (SI)

Measurement system derived from the metric system; units include: metre (m) for length, kilogram (kg) for mass, second (s) for time, ampere (A) for electric current, Kelvin (K) for thermodynamic temperature, mole (mol) for amounts of substance.

Lagrangian GPS drifter

Floating device used to determine current speed, direction and dynamic in a water body.

Land use

The human modification of natural environment or wilderness into built environment, such as fields, pastures, and settlements. Land use refers to the total of arrangements or sets of social and economic activities in a certain area (e.g., grazing, timber extraction and conservation). The type of land use determines the level of evapotranspiration of this land as well as its function as a GHG source or sink. When estimating pre-impoundment *GHG emissions*, the chosen *reference* site should have similar land uses as well as similar climatic conditions.

Life-cycle assessment (LCA)

A life-cycle assessment (also known as 'life-cycle analysis', 'ecobalance', and 'cradle-to-grave analysis') is the investigation and evaluation of the environmental impacts of a given product or service caused or required by its existence. An estimation of *net GHG emissions* of a reservoir needs to assess changes in emissions throughout the life-cycle of a reservoir. For new reservoirs, high *gross emissions* may occur because of the

decay of impounded *biomass* and emissions resulting from the construction phase. These values, however, may change as the reservoir ages.

Lifetime

A general term used for various time scales characterising the rate of processes affecting the concentration of trace gases. For new reservoirs, high *gross emissions* may be observed and longer measurement periods (up to 10 years) may be needed to account for the emission changes over the reservoir's lifetime.

Macrophyte

Rooted plant that grows in or near water.

Methane (CH₄)

A chemical compound with the chemical formula CH₄. It is a gas at normal temperature and pressure. It is a naturally occurring *GHG*, a main component of natural gas, and an end-product of animal husbandry and agriculture. Methane is a relatively potent greenhouse gas, presenting a global warming potential 21 to 25 times stronger than CO₂ (over a 100-year period).

Methanotrophic bacteria

Bacteria that feed on CH₄ and oxidize it to CO₂ as an end-product.

Methane (CH₄) oxidation

Process by which CH₄ is oxidised to CO₂ and which occurs in *aerobic* soils.

Methanogenesis

Production of CH₄ through respiration by anaerobic bacteria and microbes present in the *anoxic* layers of a water body, after feeding on the *detritus* of organic matter (OM).

Net GHG emissions (see *GHG status of a reservoir*)

Nitrification

An *aerobic* process in which bacteria change the ammonia, organic nitrogen and decomposed matter in water into oxidized nitrogen (nitrate), thus increasing the likelihood of N₂O emissions of this water body. De-nitrification describes the conversion of nitrate into nitrite, then to N₂O and finally to nitrogen gases. This process happens in the slightly *anoxic* upper layer of sediment.

Nitrous oxide (N₂O)

A chemical compound with the formula N₂O (commonly known as laughing gas), which is an oxide of nitrogen. It is a naturally occurring *GHG* produced through bacterial *nitrification* and *de-nitrification* processes. The global warming

potential of N_2O is 310 times stronger than that of CO_2 (over a 100-year period).

N_2O (see *Nitrous oxide*)

Organic matter (OM)

Carbon-containing residues of plants and soils. OM enters a reservoir via groundwater, inflow, erosion of the littoral zones and decay of plant material in the impounded area. Decomposition of OM in water results in release of its carbon as CO_2 and CH_4 fluxes. In the years following impoundment, increased CH_4 fluxes are sometimes recorded, since decay of OM in water happens in anoxic conditions, as opposed to natural decomposition of OM into CO_2 , which occurs in oxic conditions.

Oxic

Describes conditions in water and its sediments in which oxygen is present and that are often a source of CH_4 oxidation.

Oxygen sensor

An electronic instrument to measure the oxygen content of a gas or liquid.

Partial pressure gradient

Physical quantity that describes in which direction and at what rate the pressure changes most rapidly around a particular location.

Particulate organic carbon (POC) (see *Carbon mass flow*)

Periphyton

Microscopic plants and animals that are firmly attached to solid surfaces such as rocks, logs, pilings and other structures under water.

Peristaltic pump

An instrument used for pumping fluids. The fluid is contained in a flexible tube fitted inside a circular pump casing. A rotor with a number of rollers attached to the exterior compresses the flexible tube. As the rotor turns, the part of the tube under compression closes, forcing the fluid to move through the tube.

pH

pH is a measure of the acidity of water given by its concentration of hydrogen ions (H^+). pH is measured on a logarithmic scale where $pH = -\log_{10}(H^+)$. Thus, a pH decrease of 1 unit corresponds to a 10-fold increase in the concentration of H^+ , or *acidity*.

Photo-oxidation

Oxidation of *dissolved organic carbon* in water to CO_2 under the influence of sunlight.

Photosynthesis

The process, driven by solar energy, by which atmospheric CO_2 is fixed by plants and algae for the *primary production of OM*, with oxygen as a by-product.

Phytoplankton

Form of aquatic plant that feeds by *photosynthesis*.

Pressure transducer

An electric or electromagnetic instrument that uses pressure to convert one type of energy or physical attribute to another to facilitate measurements or make measurements comparable.

Primary production (of organic matter)

Production of organic compounds from atmospheric or aquatic carbon dioxide, mainly through photosynthesis, and partially through chemosynthesis.

Reference site

Region or site with *land-use* and *climate* characteristics similar to those of the reservoir area before impoundment, which are used to estimate the pre-impoundment GHG emissions of that reservoir area, and also to reveal seasonal changes. Reference sites must be identified in both the aquatic and terrestrial ecosystems to ensure that normal variations due to climate or changes in land use are taken into account and not seen as reservoir effects. Reference sites may also be used to estimate net emissions when measurements begin after reservoir impoundment

Reservoir volume

The total water availability in the reservoir. Volume can vary throughout the year, and measurements of minimum and maximum values (in $m^3 \times 10^6$) should be made.

Residence time

Average time a water molecule spends in a reservoir. Used to describe the flow rate of the water through the reservoir. Value can vary inside one reservoir.

Rhizosphere

The narrow region of soil that is directly influenced by root secretions and associated soil microorganisms.

Riparian zone

A riparian zone or riparian area is the interface between land and a water body.

Sequestration (See Uptake)**Shoreline length**

Refers to the edge of a water body. Values can vary with seasonal water variability, and measuring the minimum and maximum shoreline length is recommended.

SI (see International System of Units)**Sink (see Carbon sink)****Soil incubator**

A device used to keep soil samples at a constant temperature as part of a series of steps in the determination of GHG concentration in soil samples.

Stratification

A water body can be stratified in layers of temperatures, salinity or chemical compositions, which can act as barriers to water mixing.

Terrestrial ecosystem (see Ecosystem)**Thermistor**

Temperature-sensitive electrical resistor whose electrical resistance varies with temperature.

Total organic carbon (TOC) (see Carbon mass flow)**Turbidity**

The amount of solid particles that are suspended in water and cause cloudiness or haziness of the water. Turbidity is measured in nephelometric turbidity units (NTU).

Tygon tube

Brand name for a type of flexible tubing.

Uptake (see Carbon sequestration)**Viton**

Brand of synthetic rubber commonly used for rings or septums in chemical analysis instruments.

Water basin (see Basin)**Water current meter**

An instrument used to measure the speed and direction of a current in a river or water body.

Water cycle (see Hydrologic cycle)**Watershed (see Basin)****Bibliography**

IPCC, 2007: *Climate Change. Impacts, Adaptation and Vulnerability*, M. Parry, O. Canziani, J. Palutikof, P. Van der Linden, C. Hanson (Eds.), Cambridge University Press, Cambridge and New York, 79 pp.

IPCC, 2007: *Climate Change 2007. The Physical Science Basis*, S. Solomon, D. Qin, M. Manning, M. Marquis, K. Averyt, M.M.B. Tignor, H.L. Miller Jr., Z. Chen (Eds.), Cambridge University Press, Cambridge and New York, 129pp.

Matvienko B.: *The Carbon Cycle in Hydroelectric Reservoirs and the Greenhouse Effect*, in: Rosa L.P., Dos Santos M.A., Tundisi J.G. (Eds.): *Greenhouse Gas Emissions from Hydropower Reservoirs*. COPPE/UFRJ, Rio de Janeiro, 2004.

Tremblay A., Varfalvy L., Roehm C., Garneau M.: *Greenhouse Gas emissions – Fluxes and Processes. Hydroelectric Reservoirs and Natural Environments*. Springer, Berlin Heidelberg New York, 2005.

As climate change takes a central position in decision making at all levels, the need to quantify the greenhouse-gas (GHG) status of human activities assumes ever more importance. In the case of water management there is a need to determine the GHG status of freshwater reservoirs; that is, assessment of any change in GHG fluxes brought about by the creation of a reservoir.

This publication is a key outcome of a multi-year process, the UNESCO /IHA GHG Status of Freshwater Reservoirs Research Project. It aims to address the above need by providing definitive guidance on measurement and quantification of emissions resulting from the formation of reservoirs. It sets out the concepts and processes involved in making such measurements, the approach to conducting field measurements, as well as guidance on calculating results. The methodology set out is applicable worldwide, for all climate types and reservoir conditions.

As such, this publication provides all the tools required to determine net GHG emissions in a selected set of reservoirs, with the intention that these results will be utilised to develop predictive tools that will in future avoid the necessity of such intensive field measurements.

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