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Guidelines for Surface Water Quality Monitoring in Small Agricultural Watersheds

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Guidelines for Surface Water Quality Monitoring in Small Agricultural Watersheds.

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FOREWORD SURFACE WATER QUALITY MONITORING IN SMALL AGRICULTURAL WATERSHEDS

Changes in agri-environmental strategies and government funding of water quality protection in agricultural watersheds in recent years have seen funding allocated specifically to projects at the small watershed scale ($100 \text{ km}^2 - 10,000 \text{ ha}$ or less, with 40 to 80 farms). Efforts are often focused on such watersheds if there are reports of problems associated with cyanobacteria (blue-green algae), or if the farm area exceeds 50% of the total watershed area, with a high proportion of annual crops.

A number of government financial assistance programs are available to help producers make changes to their practices to reduce their impact on water quality. Some programs also provide funding to businesses for the delivery of ecological services. However, the analysis of these programs reveals that they are often evaluated on the basis of the specific measures implemented (e.g., number of kilometres of riparian buffers created), but seldom on the basis of the results obtained in terms of actual water quality improvements.

Various provinces operate water quality monitoring networks. In Quebec, the Department of Sustainable Development, Environment, Wildlife and Parks (MDDEFP) runs a relatively extensive network of sampling stations on the main bodies of water. Water quality results from these stations are available only on request and their use is controlled.¹ In addition, these data cover only major bodies of water and are generally taken from stations located at the mouths of rivers, which means that the data cannot be used to specifically target the watersheds of smaller rivers that could pose particular problems.

For some time now, a number of watershed organizations have been conducting surface water quality monitoring at a smaller scale (i.e., at the subwatershed scale). In addition, some water quality monitoring projects are funded under the Quebec government's 2007-2017 blue-green algae action plan. The objective of these projects is to identify problematic streams and the factors contributing to their deterioration, and to measure the effects of remediation efforts. The results of such initiatives will be useful only if they are scientifically sound. The findings will have to be produced in a sufficiently uniform manner to permit comparisons among studies and over time. In addition, the users of the data must have the necessary tools to allow for an informed interpretation.

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¹ Only streamflow data are available online. More detailed analyses of specific bodies of water, such as Missisquoi Bay, or of pesticide monitoring in specific rivers, are occasionally released (Giroux 2010). In 2005, MDDEFP published an assessment of the phosphorus loads of major Quebec rivers (Gangbazo et al. 2005). In the United States, data can be accessed from existing stations online. Environment Canada has developed a management tool called ENVIRODAT; however, very few data are currently available online. In Quebec, water quality results are stored in the aquatic environment quality database (BQMA). Users who obtain data from the BQMA cannot, at any time or in any way, disseminate the data to a third party without prior written permission from *MDDEFP*.....Users undertake to inform the DSEE of the dissemination of publications produced using the data. Source: Data file from BQMA.

Initiative of Agriculture and Agri-Food Canada

The measurement of water quality involves the use of complex methods that sometimes require significant resources and expertise that is not widely available. Watershed restoration projects have been undertaken in recent times, mobilizing these resources, but such initiatives are few and far between. The complexity of the methods used for data collection and for the interpretation of results could limit the use of these techniques in small watershed restoration projects.

Agriculture and Agri-Food Canada is currently conducting a series of projects aimed at compiling various water quality monitoring methods in order to identify those that can be adapted to the small agricultural watershed scale and that meet the criteria of simplicity, effectiveness and low cost. The methods should make it possible to assess the state of a stream over time and to target those agricultural streams that pose real water quality problems and that contribute significantly to the loss of the use of certain rivers or lakes. The methods should also make it possible to measure the performance of farms in protecting the quality of streams that flow across their property.

In an industrial context, water quality monitoring can generally be conducted at the end of a wastewater pipe. By, contrast, in the agricultural sector pollution is diffuse in nature (nonpoint source), which makes it difficult to ensure targeted action and to reliably and effectively assess the results obtained. Water quality monitoring requires a knowledge of the watershed and of stream hydrology, selection of the parameters to be analyzed (phosphorus, nitrates, sediments, etc.), selection of sampling sites, and access to reliable and easy-to-use collection equipment that can be installed at several key locations in small agricultural watersheds.

This document provides a summary of the relevant information for each of these aspects. It is not intended to be a simple how-to guide to water quality monitoring, but rather a summary of the key information required to produce such a guide. It may be used for training agricultural sector stakeholders.

A scientifically relevant and valid water quality monitoring approach demands a sound knowledge of sometimes complex concepts and the use of rigorous techniques. There is a vast amount of technical and scientific information on water quality monitoring processes. Our objective was to focus on the key points for which an understanding is essential, and that form a common language that must be mastered by those involved in implementing such processes and by users of water quality monitoring data who wish to interpret this information in an informed manner. This introductory document is intended to be accessible and concise. It will enable users to assess the measures required to implement rigorous water quality monitoring. For more complex situations or cases requiring a more detailed discussion of certain technical concepts, interested parties are invited to consult the references listed in the bibliography.

This project involves the collaboration of two major Quebec partners: the Quebec Department of Agriculture, Fisheries and Food (MAPAQ) and the Quebec Department of Sustainable Development, Environment, Wildlife and Parks (MDDEFP).

The techniques presented in this paper can be used for small-scale agricultural watersheds regardless of their location in Canada. The examples of initiatives discussed in this paper come from across Canada, but mostly from Quebec, where this study originated.

INTRODUCTION OBJECTIVES OF WATER QUALITY MONITORING PROTOCOLS

All water quality monitoring projects necessarily involve the development of monitoring protocols, which set out the steps that must be taken to produce rigorous and reliable analysis results. A monitoring protocol includes, but is not limited to, the following steps: defining the objectives; characterizing the body of water to be analyzed; identifying the physical, chemical, biological and/or bacteriological parameters (or measurement indicators) to be given priority in the analyses; developing a sampling strategy; and finally analyzing the samples collected. Although these steps should typically be included in any water quality monitoring protocol, it is important to bear in mind that there is no one standard protocol. At each step, choices must be made that are seldom the same from one protocol to the next and that will make the protocol specific to the initiative concerned.

Critical importance of the objectives of a monitoring protocol

What parameters (indicators) will be analyzed? Where will the sampling sites be located? What sampling schedule and frequency will be used? How will the data be analyzed? In order to answer these questions, the objectives to be achieved by the water quality monitoring process must be identified at the outset.

Examples of the objectives of a monitoring protocol can be found in the literature.² Although these examples can serve as a reference in the development of a specific protocol, they cannot simply be imported wholesale into the protocol. The objectives of a project must be clearly adapted to the hydrographic regime of the water body to be evaluated, to the type of actions considered and to the available resources. There is no automatic procedure for defining the objectives, and project leaders have a critical role to play in this regard. The precision of the information sought, as formulated in the objectives, will shape all subsequent stages of the water quality monitoring protocol.

Various objectives can be established and can be modified or grouped together to form the basis of a specific monitoring project. They include:

- identifying contaminated streams and the pollutants involved; identifying the water uses that are compromised;
- verifying the contribution of one stream to the pollutant load of another stream into which it flows;
- determining the causal factors involved in the degradation of water quality;
- assessing the effect of changes in riparian zone management practices on the monitored stream.

A number of objectives are set out in the text box below. They will be discussed later in the document to illustrate the monitoring protocols that can be associated with them.

² AAFC, 2004. *Watershed Monitoring: An Introduction to Water Sampling. Reference Guide*. 32 p. http://www4.agr.gc.ca/AAFC-AAC/display-afficher.do?id=1259245521253&lang=eng

U.S. EPA, 1997. Volunteer Stream Monitoring: A Methods Manual. 4503F. EPA 841-B-97-003. United States Environmental Protection Agency. Office of Water. November 1997 http://water.epa.gov/type/rsl/monitoring/vms22.cfm

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WATER QUALITY MONITORING OBJECTIVES

An overview of the most common objectives is provided in the following pages. Note, however, that this list is not exhaustive.

Monitoring of uses

The monitoring of potential water uses is the most common objective. It is the objective used in the Réseaurivières monitoring program run by the Quebec Department of Sustainable Development, Environment, Wildlife and Parks. This objective involves determining whether the water of a stream can be used for the usual purposes. These uses can obviously differ, depending on the stream in question. Since all streams are potentially living corridors, the one use that should be systematically measured is the maintenance and enhancement of aquatic life. However, depending on the type of stream, there are other potential uses, such as drinking water consumption, irrigation, swimming, fishing and leisure activities. Water quality monitoring should provide answers to the following questions: Does the water quality allow for swimming? Can water from the stream be used for irrigating fields? What is the stage of eutrophication of the stream? Is the water quality sufficient to maintain aquatic life similar to what would be found in a pristine or relatively undeveloped area?

Monitoring of the contribution of a watershed

This type of monitoring consists of determining the pollutant load of a stream relative to other streams that flow into the same body of water and typically focuses on only a few indicators simultaneously. Monitoring of the phosphorus loads of the various tributaries of Lake Champlain, both in Quebec and Vermont, is an example. This approach can be used to identify areas where efforts must be stepped up to reduce loading to the lake.

Identification of factors responsible for deterioration of water quality

Water quality monitoring can be undertaken to establish the causal factors associated with water quality degradation. In this case, the focus is on indicators that can provide information on the impact of the main agricultural practices, such as fertilizer and pesticide use, and tillage.

Monitoring of the impact of watershed restoration practices

This type of monitoring, when it must be carried out within a short time period (less than 5 years), requires specific experimental designs that can be used to differentiate variations associated with changes in practices from variations due to other sources (seasonal variations, etc.).

A number of research projects aimed specifically at assessing the impacts of changes in agricultural practices in small watersheds are currently under way. In agricultural areas, such projects typically involve monitoring two streams in "twin" watersheds (similar in terms of hydrology). One of the watersheds is considered the control, and no protection practices are carried out in that watershed. In the other watershed, farmers implement beneficial management practices. Water quality monitoring using several indicators is carried out over several years at the mouths of the two watersheds. The objective is to obtain sufficient data in a relatively short period of time (3 to 5 years) to be able to detect fine variations using specific statistical analyses. It is often difficult to find "twin" watersheds. Therefore, in order to be able to measure the difference between the actual effects of actions taken and the differences in "behaviour" of the two watersheds, it is important to first conduct a detailed characterization of the watersheds and to have a sufficiently long reference period to be able to subsequently detect changes in water quality associated with agricultural practices.

Establishing realistic objectives requires knowledge of water quality indicators and measurement methods

The objectives of a monitoring protocol determine the information that needs to be collected, i.e., the aspects of the body of water that will be examined and measured, namely the water quality indicators. Each indicator requires a specific sampling and analysis method. Knowing these indicators, the information they can or cannot provide, the methodological requirements and the associated costs is critical to defining realistic objectives adapted to the situation at hand.

It is therefore important to attempt to determine what indicators will provide the most comprehensive overview of the information sought, at an affordable cost. This is particularly critical in the case of small agricultural watershed restoration projects that have limited financial and human resources. The water quality indicators are the main components of water quality monitoring protocols. Once knowledge of these indicators has been acquired, realistic objectives can be identified and rigorous and realistic monitoring protocols can be developed. Such knowledge is also essential for making full use of the data.

This report is divided into three sections, each of which focuses on one category of water quality indicators: physicochemical and bacteriological, biological and hydrological. We will begin by defining each group of indicators and describing the minimum level of precision required for the sample collection and analysis methods for each group of indicators.³ We will then identify the objectives that may be associated with these indicators.

³ The categories of indicator groups were not determined on the basis of the material nature of the indicators. Hydrologic indicators, for example, obviously have a physical nature, but they are not referred to as physical indicators. The criterion that we retained and that is essentially the same as that adopted by MDDEFP refers instead to distinct aspects of a body of water: indicators that measure changes in the physical, chemical and bacteriological composition of the water; indicators that can be used to assess changes in the quantity and diversity of plant and animal species; and lastly, so-called indirect indicators (hydrographic regime), which are useful and sometimes even necessary for providing insight into the monitoring results.

SECTION 1 PHYSICOCHEMICAL AND BACTERIOLOGICAL WATER QUALITY INDICATORS

1.1 IDENTIFICATION OF PHYSICOCHEMICAL AND BACTERIOLOGICAL INDICATORS

1.1.1 DEFINITION OF INDICATORS

Physicochemical and bacteriological indicators play a key role in water quality monitoring, with most studies using one or more of these indicators (sometimes grouped in the form of indices). Essentially, they measure changes in the physical, chemical and bacteriological composition of the water, associated *primarily* with loadings from stream environments. In agricultural landscapes, physicochemical and bacteriological changes are caused by loadings of nutrients, such as nitrogen and phosphorus, fecal bacteria, suspended matter and pesticides. The presence of these elements in surface water in certain concentrations indicates a potential for degradation.

Each of the physicochemical and bacteriological indicators, as well as the mode of action of the contamination process resulting in its entry into a stream, is described in the box below.

Phosphorus

The presence of excessive phosphorus levels in a stream indicates a potential for accelerated eutrophication.¹

Phosphorus, like nitrogen, has a fertilizing effect on aquatic plants. However, in freshwater, it is generally the absence of phosphorus that first limits plant growth. When phosphorus is added to water, aquatic plants, particularly those with the ability to fix nitrogen from the air (such as cyanobacteria), undergo prolific growth, thereby reducing oxygen levels in the water. Nitrogen does not have significant impacts unless phosphorus levels are sufficiently high. By contrast, in the marine environment, nitrogen is the limiting factor (CCME 2003).

Although it plays a role in eutrophication, phosphorus is not toxic to humans or animals.

The measurement of total phosphorus is used to determine the risks of eutrophication. Researchers use different forms of phosphorus as indicators, including orthophosphates or "reactive phosphorus," hydrolysable phosphates and dissolved or particulate organic phosphates. Dissolved phosphorus is the form found in filtrate, while particulate phosphorus is the form that stays on the filter. Dissolved reactive phosphorus is more readily available to aquatic plants and is therefore a more direct eutrophication factor. Particulate phosphorus can also be made available to plants, but it is a slower process (Berryman et al. 2006). The differences between particulate and dissolved phosphorus are of particular interest in research on the mechanisms of phosphorus transport from soil to streams.

Phosphorus is an indicator of the potential transfer of fertilizers to streams.

¹ Eutrophication is the nutrient enrichment of waters that stimulates an array of symptomatic changes, that can include increased production of algae and macrophytes that are considered undesirable and that interfere with water uses (OECD, cited in Glavez-Cloutier et al. 2002).

Nitrogen

Like phosphorus, nitrogen is an essential nutrient for aquatic plant growth. **Therefore, it too is an** *indicator of eutrophication.* While phosphorus is more typically the limiting factor in freshwater, nitrogen is the key limiting factor in the marine portion of estuaries, where excess nitrogen inputs are particularly problematic (increased primary production, reduced oxygen and sudden fish mortality).

Nitrogen is found in water bodies in both organic and inorganic forms. The breakdown of organic nitrogen (the nitrogen found in amino acids and proteins) by certain microorganisms produces various inorganic forms. The first form produced is ammonia (NH3-N), which is then converted by certain bacteria to nitrites (NO2-N) and then nitrates (NO3-N) (denitrification).

It is this inorganic form (nitrate) that is used by aquatic plants. However, to obtain a good idea of the eutrophication potential, it is important to measure all forms of nitrogen present in the water (total nitrogen).

In addition to their impact on eutrophication, the three inorganic forms of nitrogen—*nitrates (NO3-N), nitrites (NO2-N) and ammonia nitrogen (NH3-N)*—*are toxic to aquatic life and to humans (consumption of drinking water) (Table 1).*

Nitrogen, like phosphorus, is an indicator of potential fertilizer loading to streams. In particular, elevated concentrations of ammonia nitrogen from agricultural sources are indicative of fertilizer loading (mineral and organic) to streams.

Suspended solids⁴

Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton and other microscopic organisms (CCME 2002). Suspended solids correspond to all matter that will not pass through 1.2- μ m or 0.45- μ m pore size filters (Centre d'expertise en analyse environnementale du Québec, 2008).

When present in water in excessive concentrations, suspended solids have an impact on the aquatic ecosystem. In 2002, the CCME produced a summary of various studies that examined the impacts of excessive suspended solids on aquatic life, including the modification of algae production, changes in invertebrate populations, and effects on fish (e.g., gill obstruction and abrasion, habitat alteration).

Suspended solids in streams can come from various sources, including shoreline erosion, soil erosion, road work, dredging, and forestry activities.

⁴ The presence of suspended matter in water can also be assessed by measuring turbidity (water transparency). In the laboratory, turbidity is measured using a nephelometer, which measures the intensity of light scattered by suspended solids. In the field, turbidity can be measured using a turbidimeter. The transparency of the water can also be measured using a simple and inexpensive technique, which involves lowering a Secchi disk into the water until it can no longer be seen. It is possible to establish correlations between these different indicators. However, there is no universal equation linking turbidity and SS concentrations, and measurements must therefore be taken at the outset to establish the correlation equation (Birgand 2004, Thackston et al. 2000).

Fecal coliforms

The presence of excessive concentrations of fecal coliforms in surface waters has a direct impact on the use of the water for human consumption, swimming or irrigation of crops.

Fecal coliforms are indicators of fecal contamination by humans and other warm-blooded animals. Wastewater discharges (municipal, industrial or domestic) are the main source of fecal coliform contamination. In agricultural areas, fecal coliforms can indicate a potential transfer of pathogens from manure and slurries to streams.

Pesticides

Pesticides in surface waters are generally monitored independently of other indicators in a separate monitoring program. Because of the wide variety of pesticides used and the very high cost of the analyses, specific sampling strategies are required. Unlike the other physicochemical parameters, pesticides are not systematically monitored under the Réseau-rivières program. Studies conducted by MDDEFP generally target specific watersheds based on the crops present in the area. Since 1992, four streams whose watersheds contain large areas devoted to field crops (corn, soybeans) have been the subject of monitoring: the Chibouet River (Yamaska River watershed), the Rivière des Hurons (Richelieu River watershed), the Saint-Régis River (direct tributary of the St. Lawrence River) and the Saint-Zéphirin River (Nicolet River watershed) (Giroux 2010).

Short-term studies (over several years) have also been conducted in streams draining specific crops: vegetable crops, orchards, blueberries.

A very large number of pesticides are monitored. In a study conducted from 2005 to 2007 in a stream draining primarily vegetable crops, over 70 different pesticides were monitored (Giroux et al. 2010). In another study that did not target any specific crops, but rather agricultural watersheds on the north shore of the St. Lawrence River, 54 different pesticides were analyzed (Giroux 2007).⁵

Excessive concentrations of pesticides in water have an impact on the quality of water for human consumption, on aquatic life and on irrigation.

1.1.2 CHOICE OF THRESHOLD VALUES

The presence of physicochemical and bacteriological parameters in water does not necessarily mean they have an adverse effect on water quality. A water quality measurement strategy must provide for the quantification of these parameters and their assessment against threshold values that are considered to be scientifically significant in terms of the associated impacts on water quality.

⁵ Pesticide monitoring is also carried out by the Water Quality Monitoring and Surveillance Section of Environment Canada's Science and Technologies Branch.

Scientifically defined threshold values

Water quality data obtained for a specific body of water (concentrations of physicochemical and bacteriological elements) are generally compared with what are referred to as threshold concentrations (i.e., scientifically determined levels beyond which water degradation processes begin that can eventually limit or eliminate one or more water uses). Government authorities use these reference values by integrating them into regulations or guidelines.

In Quebec, quality criteria have been established for over 300 contaminants that may affect water uses (MDDEP, 2009).⁶

In this list of contaminants, MDDEFP identifies four basic water uses and, for each, indicates the physicochemical parameters (contaminants) that can affect them and at what concentration. The four basic uses are human consumption of water and aquatic organisms, maintenance of the typical aquatic life of streams, protection of wildlife that consumes aquatic organisms and protection of recreational uses (involving direct or indirect contact with water) and aesthetics of streams.

Tables 1 and 2 present the threshold concentrations established for the main contaminants typically found in agricultural areas, and the uses of streams that may be affected.

⁶ These criteria are based on various studies conducted by MDDEFP and by other organizations, such as the Canadian Council of Ministers of the Environment, Health Canada, the U.S. Environmental Protection Agency (EPA), and the World Health Organization. In Canada, **the Canadian Council of Ministers of the Environment** is responsible for proposing threshold values. It has published guidelines for recreational water quality and aesthetics, for the <u>protection of aquatic life</u> and for the protection of agricultural water uses (irrigation and livestock watering). For each of these uses, threshold concentrations for various elements (nutrients, pesticides, etc.) are proposed. <u>http://cegg-rcqe.ccme.ca/?lang=en</u> (last accessed December 6, 2011).

Health Canada has published the *Guidelines for Canadian Drinking Water Quality* on behalf of the Federal-Provincial-Territorial Committee on Drinking Water (CDW). These guidelines are available online at <u>http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2010-sum guide-res recom/index-eng.php</u> (last accessed December 6, 2011).

In 2009, **Environment Canada** published a report on the National Agri-Environmental Standards Initiative (NAESI). The objective of the initiative was to develop *national non-regulatory agri-environmental performance standards*. Two types of standards are proposed: ideal performance standards (IPS), which *specify the desired level of environmental state needed to maintain ecosystem health*; and achievable performance standards (APS), which *specify the level of environmental quality that can be achieved using beneficial management practices (BMPs)* (Bowerman et al. 2009). With respect to the protection of freshwater, the report proposes standards that, on the basis of the indicators, vary depending on the size of the streams and the ecosystem in which the stream is located. For example, in the large Mixedwood Plains ecosystem (Ontario and Quebec), the recommended IPS for total phosphorus is 0.024 mg/L for small and medium streams and 0.019 mg/L for large streams. The report also proposes standards for total nitrogen, nitrates, total suspended solids, turbidity, average *E. coli* concentration and various pesticides (Bowerman et al. 2009).

	Preventi	on of contamination	Pro	tection of aquatic life	Α	В
	Water and aquatic organisms	Aquatic organisms only (not a source of drinking water)	Acute effect	Chronic effect		
Ammonia nitrogen (mg-N/L)	0.2 - 1.5	No guideline	Variable depending on pH and temperature	Variable depending on pH and temperature	No guideline	No guideline
Nitrates (mg-N/L)	10	No guideline	No guideline	2.9 (this quality criteria is under review)	No guideline	No guideline
Nitrites (mg-N/L)	1	No guideline	0.06 (variable depending on chloride level)	0.02 (variable depending on chloride level)	No guideline	No guideline
Total phosphorus (mg-P/L)	No guideline	No guideline	No guideline	0.02 for streams emptying into lakes where environmental conditions are not problematic. 0.03 in rivers and streams to limit eutrophication.The guideline can be lower in certain cases (eutrophication)(more details on the web site)	No guideline	0.02 for streams emptying into lakes where environmental conditions are not problematic. 0.03 in rivers and streams to limit eutrophication.
Turbidity (NTU)	No guideline	No guideline	The guideline for clear flow periods is a maximum increase of 8 NTU over background levels.	The guideline for dry weather periods is an average maximum increase of 2 NTU over background levels.During periods of high flow (rain, snowmelt) or in turbid waters, the guideline is defined either by a maximum increase at any time of 8 NTU over the background level when it is between 8 and 80 NTU, or by a 10% increase over the background level when it exceeds 80 NTU at a given point in time.	No guideline	Maximum increase of 5 NTU over the background level, when it is low (< 50 NTU).
Suspended solids (mg/L)	No guideline	No guideline	The guideline for dry weather periods is a maximum increase of 25 mg/L over background levels. The guideline for dry weather periods is a maximum increase of 25 mg/L over background levels. The guideline for dry weather periods is an average maximum increase of 5 mg/L over background level when it is between 25 and 250 mg/L, or by a 10% increase over the background level when it exceeds 250 mg/L at a given point in time. This guideline applies to freshwater, estuarine and marine waters.		No guideline	No guideline
Fecal coliforms (cfu/100 mL)	1,000	No guideline	No guideline	No guideline	No guideline	200 (swimming) to 1,000

Table 1: Water quality guidelines for various parameters as a function of type of use

Source: <u>http://www.mddep.gouv.qc.ca/eau/criteres_eau/index.asp</u> (last accessed April 5, 2011) Note: These criteria apply only to surface waters. They serve as reference tools for assessing the chemical integrity of ecosystems.

A: Protection of fish-eating terrestrial wildlife; B: Protection of recreational uses and aesthetics

	Prevention of contamination		Protection of aquatic life		Protection of fish- eating terrestrial wildlife	Protection of recreational uses and aesthetics
	Water and aquatic organisms	Aquatic organisms only (no source of drinking water)	Acute effect	Chronic effect		
Atrazine (herbicide) (mg/L)	0.005 (provisional)	8.6	0.05	0.0018	No guideline	No guideline
Glyphosate (herbicide) (mg/L)	0.28 (provisional)	No guideline	No guideline	0.065 (provisional)	No guideline	No guideline
Metolachlor (herbicide) (mg/L)	0.05 (provisional)	0.034	0.11	0.0078 (provisional)	No guideline	No guideline
Metribuzin (herbicide) (mg/L)	0.08	No guideline	No guideline	0.001 (provisional)	No guideline	No guideline
Linuron (herbicide) (mg/L)	No guideline	No guideline	No guideline	0.007 (provisional)	No guideline	No guideline
Chlorpyrifos (insecticide) (mg/L)	0.09	No guideline	2.7 x 10 -5	3.5 x 10 -₅	No guideline	No guideline
Malathion (insecticide) (mg/L)	0.19	No guideline	No guideline	1 x 10 ⁻⁴	No guideline	No guideline
Diazinon (insecticide) (mg/L)	0.02	0.037	6.4 x 10 -5	4 x 10 -6	No guideline	No guideline
Chlorothalonil (fungicide) (mg/L)	0.0015	No guideline	No guideline	1.8 x 10 -4 (provisional)	No guideline	No guideline

Table 2: Water quality guidelines for various pesticides as a function of type of use*

*These are just a few of the most commonly used pest control products.

Source: http://www.mddep.gouv.gc.ca/eau/criteres_eau/index.asp (last accessed December 13, 2010)

EXPLANATORY NOTE FOR TABLES 1 AND 2

Criteria for the prevention of contamination (CPC) are established to reduce risks to human health. **For surface waters with** *a drinking water intake,* CPC are designed to protect an individual who, throughout his or her life, drinks water contaminated with a given substance in the specified concentration and eats aquatic organisms that have bioaccumulated the substance. **For surface waters with no drinking water intake**, CPC are designed to protect an individual who, throughout his or her life, eats aquatic organisms that have bioaccumulated the substance. Source: MDDEFP. http://www.mddep.gouv.qc.ca/eau/criteres_eau/fondements.htm (last accessed April 10, 2012)

Criteria for the protection of aquatic life (CPAL) are established without regard to potential impacts on humans; they are designed to protect aquatic life.

Example for nitrates: the CPC for surface waters with a drinking water intake is 10 mg-N/L; there is no CPC for surface waters with no drinking water intake; and the CPAL is 2.9 mg-N/L.

Threshold values from comparative studies

In addition to the threshold values presented above, comparative threshold values can also be used to assess physicochemical or bacteriological parameters in water. The results obtained for a given body of water are compared with the results obtained for the same indicators at a different site or at a different time. This involves selecting either another stream located in a similar watershed (similar in terms of geology, soil type, topography), or a different portion of the same stream, farther upriver. It is also possible to use the same stream at the same location, but at different times, as a basis for comparison.

There are many reasons for using comparative studies, and the information obtained will differ depending on the type of comparison. For instance, measurement data obtained for a particular stream under study can be compared with those obtained for another stream that is located in a geographically similar watershed, but that is subject to little or no agricultural, urban or forestry development pressure. For streams located in a relatively undeveloped watershed, the data show what experts refer to as background concentrations (i.e., the level or degree of contamination that could be expected in the absence of any use of the area). It is therefore possible to measure the difference between the two streams and assess the impacts of degradation associated with development activities in the more heavily developed watershed.

Data for the stream under study can also be compared with those obtained for a stream in a geographically similar watershed subject to similar agricultural pressures. If restoration practices are carried out in one of the watersheds but not in the other, the comparison will make it possible to measure the effects of the restoration efforts (paired, or twin, watersheds).

Comparisons can also be made of water quality measurement data obtained in upstream and downstream portions of a stream, or of data obtained for a given stream at different times. Such comparisons make it possible to measure the impact of the shoreline area (if it is sufficiently large) on the stream or to measure changes in water quality over time.

1.1.3 WATER QUALITY INDICES

Tables 1 and 2 above present the analysis of each indicator taken separately, indicating the value above which the concentration of that parameter will have an impact on a specific water use without affecting the other uses. In such cases, it can be concluded that there is an emerging contamination problem. But does this mean that the body of water is degraded? To reach such a conclusion, is it enough for only one water use to be compromised or must several uses be compromised? Can there be only one contaminant present or must there be several? In other words, what conclusions concerning the quality of the body of water as a whole can be drawn on the basis of the presence of one contaminant in a concentration exceeding the threshold value?

As stated at the start of this document, water is a multifaceted resource, due to its many components. The monitoring of a single indicator, albeit important for tracking a specific problem, can often be inadequate for assessing the overall state of the water body. Depending on the availability of resources, it is useful to measure more than one indicator in order to obtain a detailed assessment of the quality of the body of water. To this end, several indicators can be grouped together to create an index that can be used to classify water bodies on the basis of more than one indicator.

It is in this context that various water quality indices have been developed, such as the Water Quality Index (WQI), a Canada-wide index; the GLOBO index, developed locally by a non-governmental organization; and the *Indice de la qualité bactériologique et physico-chimique de l'eau* (IQBP), a Quebec index. The importance of a full understanding of the IQBP is twofold: first, it is the key instrument for classifying water bodies in Quebec, and second, studying the IQBP can provide a clear picture of the differences between it and other quality indices.

<u>IQBP</u>

In the late 1990s, the Quebec Department of Environment developed a bacteriological and physicochemical water quality index (IQBP) for representing water quality throughout its Réseau-rivières network. Based on this index, water bodies are grouped into five classes of water quality:

- Class A: Water of good quality that is generally suitable for all uses, including swimming
- Class B: Water of fair quality that is generally suitable for most uses
- Class C: Water of marginal quality, some uses may be compromised
- Class D: Water of poor quality, most uses may be compromised
- Class E: Water of very poor quality, all uses may be compromised

To classify a body of water, water quality is examined using <u>seven indicators</u>: fecal coliforms, ammonia nitrogen, nitrites-nitrates, total phosphorus, suspended solids, turbidity, and chlorophyll a.⁷

For each quality class listed above, threshold values for each indicator were established by a team of experts. **Table 3** presents the criteria used to assign a water body to one of the five classes.

		Class A Water of good quality that is generally suitable for all uses, including swimming	Class B Water of fair quality that is generally suitable for most uses	Class C Water of marginal quality, some uses may be compromised	Class D Water of poor quality, most uses may be compromised	Class E Water of very poor quality, all uses may be compromised
Fecal coliforms	(cfu/100 mL)	<=200	201-1,000	1,001-2,000	2,001-3,500	>3,500
Total phosphorus	(mg-P/L)	<=0.030	0.031 -0.050	0.051 -0.100	0.101 -0.200	>0.200
Ammonia nitrogen	(mg-N/L)	<=0.23	0.24 -0.50	0.51090	0.91 -1.5	>1.5
Nitrates and nitrites	(mg-N/L)	<=0.50	0.51 -1.00	1.01 -2.00	2.01 -5.00	>5.00
Suspended solids	(mg/L)	<=6	7-13	14-24	25-41	>41
Turbidity	NTU	<=2.3	2.4 -5.2	5.3 -9.6	9.7 -18.4	>18.4
Total chlorophyll a	(mg/m³)	<=5.7	5.71 -8.6	8.61 -11.10	11.11 -13.90	>13.90

Table 3: Classification of the various parameters of the IQBP

Source: Hébert Serge, MEF, 1996. Développement d'un indice de la qualité bactériologique et physico-chimique de l'eau pour les rivières du Québec. <u>http://www.mddep.gouv.qc.ca/eau/eco_aqua/rivieres/indice/IQBP.pdf</u> (last accessed November 24, 2009)

In a water quality monitoring process, the values obtained for each indicator are expressed as classes. It is important to note that the IQPB is neither a sum, nor a mean of the values obtained for each indicator. The IQBP is what is known as a minimum operator index. The lowest indicator value determines the quality class assigned to a water body. For example, if all the indicators have values corresponding to Class A, except one, which falls in Class C, the IQBP will assign the water body to Class C (water of marginal quality).

The index ensures that a certain number of basic indicators are reviewed before the water body is ranked. To be able to establish a clear diagnosis and identify a water quality problem, it is crucial to know the element or elements that result in a lower rank and not just the overall IQPB rating. The causes of poor water quality may vary widely depending on the elements covered in the classification. In addition, to be able to address the problematic elements, it is necessary to examine the results for each indicator so as to determine which ones are responsible for water quality issues.⁸

 $^{^{7}}$ According to information provided in 2010 by MDDEFP, pH, BOD₅ and dissolved oxygen saturation are generally no longer used in the calculation due to interregional variations (pH), the absence of problems noted for several years (BOD₅) and sampling difficulty (dissolved oxygen saturation).

In recent years, the IQBP has also been calculated by excluding turbidity to see whether this parameter is the only minimum operator, which would alter the interpretation of the results. At present, stream water quality classes based on turbidity are the same regardless of location and are identified by absolute figures. Turbidity varies "naturally" as a function of geology, soil type, plant cover and slope of the streams. The IQBP can therefore result in a stream being classified as poor quality simply because its turbidity is too high, even if the excessive turbidity is due to natural erosion. ⁸ The IQBP is designed to assess water quality during the summer (May to October), that is, the period when aquatic life is

most vulnerable to the effects of pollutants. The index is not designed to assess water quality during spring high water or in winter (Hebert, 1997).

Other indices may be used. Locally, the management corporation, CHARMES, an environmental protection and sustainable development firm in Sherbrooke, Quebec has developed an adaptation of the IQBP that analyzes different elements and applies more restrictive quality criteria than those used in the IQBP. According to its designers, this adaptation, called the GLOBO index, is intended to more rapidly identify stream degradation processes.

The Canadian Council of Ministers of the Environment (CCME) developed the WQI, an open index that does not define *a priori* any parameters or specific quality criteria to be used in its calculation. It permits an evaluation of the extent (scope, frequency, amplitude) to which a certain number of elements exceed the predefined guidelines (Hébert, 2005). Each province can select elements to be included in the index calculation along with the quality guidelines for each element. Since the WQI is not a minimum operator index, exceedances of water quality guidelines for a specific parameter may, to a certain extent, be compensated for by better results for other parameters. Therefore, this index may mask specific problems related to a given parameter.

More information on the GLOBO and WQI indices is provided in **Annex 1**. **Table 4** presents a summary comparison of the three indices.

WQI	IQBP	GLOBO
Canada-wide index	Quebec index	Local index: Sherbrooke
Elements measured and quality criteria used in the calculation:	Elements measured and quality criteria used in the calculation:	Elements and quality criteria used in the calculation:
To be determined by the user	Predetermined	Predetermined Turbidity (NTU)
Pesticides can be included in the indicators used.	Turbidity Suspended solids Fecal coliforms Ammonia nitrogen Nitrites-nitrates Total phosphorus Chlorophyll <i>a</i>	Suspended solids Fecal coliforms Nitrites-Nitrates Total phosphorus Total nitrogen pH Dissolved oxygen saturation Total organic carbon Transparency
Not a minimum operator ^a	Minimum operator index ^a	Minimum operator index

Table 4: Comparison of three water quality classification indices (WQI, IQBP, GLOBO)

^a: With a "minimum operator" method, if all indicators used in calculating the index have acceptable values (lower than the threshold values) except for one, the latter is used to determine the final water quality index class.

1.1.4 USE OF INDICES IN WATER QUALITY MONITORING IN AGRICULTURAL AREAS

The use of an integrative index can be a simple way to present physicochemical water quality results. This type of index makes it possible to identify problematic streams at a single glance. However, it is important to understand how the index works in order to be able to properly interpret the results.

It is essential that results provided in the form of an index be systematically accompanied by the parameters and guidelines used in calculating the index, specifying those that pose problems. The measures to be taken to correct a problem will differ depending on the problematic parameters that are identified.

The choice of an index is up to the individuals responsible for the water quality monitoring project concerned. However, the IQBP, which is used at the provincial level, provides a better basis for monitoring the quality of a given body of water .

1.2 MONITORING PROTOCOLS USING PHYSICOCHEMICAL AND BACTERIOLOGICAL INDICATORS

In this section, we discuss in detail the various components of a water quality monitoring protocol. A protocol defines the entire proposed water quality monitoring strategy. In addition to the objectives sought by the monitoring project, the protocol contains the list of indicators to be measured, and the rationale for their use based on the objectives to be achieved. Depending on the indicators used, the protocol will specify the planned sampling and data collection methodology, and the analysis and interpretation techniques that will be applied to the data collected. The content of a protocol is specific to each water quality monitoring project.⁹

1.2.1 SAMPLING STRATEGY

The sampling strategy is developed on the basis of the objectives sought. **Table 5** presents a summary of the essential aspects (basic indicators, sampling location and schedule) of a water quality monitoring strategy for an agricultural area based on the objectives sought.

As shown in **Table 5**, the sampling strategy used to assess water quality as a function of various uses is relatively simple. It involves the regular collection of discrete samples, capturing both low flows and rainfall events.¹⁰ The sampling schedule can be limited to the summer period. However, if the objective is to determine, for example, the impact of restoration practices, it is necessary, in the context of nonpoint source pollution, to capture high flow periods and to establish year-round monitoring. The latter type of monitoring (contribution of a watershed and effect of practices) cannot be carried out without continuous streamflow measurements.

⁹ This section does not address pesticides. Pesticide monitoring requires sampling strategies adapted to the crops in a watershed. For more information, visit the following website:

http://www.mddep.gouv.qc.ca/eau/eco_aqua/pesticides/index.htm#prog_echantillonnage (last accessed March 20, 2012)

¹⁰ Sampling strategy to calculate the IQBP

The summer period (May to October) is considered the appropriate period for sample collection. It is generally the period during which water uses are the most significant. To calculate the IQBP at a given station, MDDEFP uses a minimum monitoring period of 3 years with samples collected every month for six months (May to October) for a minimum of 18 samples. Since sampling is regular and systematic, the use of data collected over a 3-year period ensures a balance between samples collected in low flow periods and samples collected during rainy periods. As previously mentioned, the IQBP was not designed to assess water quality during spring high waters or in winter. The sampling schedule is therefore adapted accordingly, but there is a high risk of missing major flood events, which are a significant factor in nonpoint source pollution. A shorter monitoring period with a smaller number of samples decreases the precision of the measurements. If samples are collected primarily during low flow periods, the effect of loading to streams during rainfall events is not taken into account sufficiently, in spite of the fact that such loadings form the bulk of nonpoint source pollution. For monitoring over a period of less than 3 years, MDDEFP proposes a minimum of 9 samples collected during the summer with a minimum of 3 samples during rainy periods, in order to assess the water quality of a given stream.

Objectives of water quality measurements	Essential indicators to be measured	Location of sampling points	Schedule and frequency of sampling*
- Enrichment of waters pron	noting acceleration of eutro	tural areas have two main types of impac ophication processes umans that come into contact with water.	ts:
Monitoring of uses Protection of aquatic life	Eutrophication - Total phosphorus - Total nitrogen - Suspended solids or turbidity <u>Toxicity</u> Nitrates Ammonia nitrogen Suspended solids Pesticides	The samples will be taken at sites where the state of the aquatic environment is to be assessed. The downstream portion of the watershed under study is generally a good site because it receives all waters that flow into the watershed. Upstream monitoring can make it possible to see whether the water quality is similar or whether there are significant differences.	May to October The frequency of sampling can be fixed (every two weeks) but it is important to capture rainfall events (and therefore to add samples if necessary)
Monitoring of uses Protection of nearby recreational or water-based activities	Eutrophication - Total phosphorus - Total nitrogen - Suspended solids or turbidity <u>Toxicity</u> Fecal coliforms Pesticides	Near swimming areas This is not intended to replace the water quality monitoring conducted by beach authorities, but to provide an idea of the state of a stream in terms of this objective.	May to October (main period of use of the bodies of water) The frequency of sampling can be fixed (every two weeks) but it is important to capture rainfall events (and therefore to add samples if necessary)
Monitoring of uses Protection of a drinking water intake (livestock watering, cleaning of instruments that come into contact with marketed food products, etc.) or irrigation intake	Toxicity Fecal coliforms Nitrates-nitrites Ammonia nitrogen Pesticides	Near the water intake	During the entire period that the water intake is in place and is used. The sampling frequency can be fixed (every two weeks) but it is important to capture rainfall events (and therefore to add samples if necessary)
Monitoring of the impact of restoration practices Monitoring of the contribution of a watershed	(Fecal coliforms) Total phosphorus Total nitrogen Suspended solids Pesticides Flow Rainfall	Downstream of the watershed	Year round Capturing rainfall events is critical for monitoring nonpoint source pollution. A fixed sampling schedule can complete the picture.

Table 5: Examples of monitoring strategies based on the objective sought

This table is based on information provided by Hébert et al. (2000), EPA (1997), and Birgand (2009). *Note: It may also be important to adjust the sampling schedule based on the timing of pesticide and/or fertilizer applications in fields.

1.2.2 SAMPLE COLLECTION

The Centre d'expertise en analyse environnementale du Québec (CEAEQ) provides information on sample collection. Part of the information is reproduced in **Table 6** below.

Table 6: Sample collection

Parameter analyzed	Sample volume to be collected	Type of container	Sample storage and time between collection and analysis**
Suspended solids	500 mL 1 L for greater precision*	Plastic or glass	4°C 7 days
Fecal coliforms	250 mL	Sterile wide-mouth glass or polypropylene container Maintain asepsis during sample collection	Thermal insulation Refrigerated during transport 48 hours
Nitrogen (total nitrogen, nitrates, nitrites, ammonia nitrogen)	250 mL	Plastic or glass	4°C 48 hours The sample can be stored longer if it is filtered and acidified
Total phosphorus	500 mL	High-density polyethylene (HDPE)	4°C 48 hours

* Only a volume of 1 L provides reliable information for determining whether the water is of good quality for this parameter according to the IQBP criteria. See the section on standard laboratory analyses for explanations.

** The sample storage time varies depending on the preservatives present in the bottles; it must be validated with the laboratory.

Source: Méthodes d'analyses. Centre d'expertise en analyse environnementale du Québec (CEAEQ). <u>http://www.ceaeq.gouv.qc.ca/methodes/chimie_inorg.htm</u> (last accessed May 11, 2010)

MDDEFP has published a guide entitled *Suivi de la qualité des rivières et petits cours d'eau*, which provides detailed information on stream sampling techniques (Hébert et al. 2000). It is very important to consult this guide before collecting samples.

1.2.3 SAMPLE ANALYSIS METHODS

The samples that are collected can be analyzed in one of two ways: either in a laboratory using standard procedures (**standard laboratory analyses**) or in the field following simplified procedures (**simplified field analysis**). The first option reduces variations in measurements that are associated with sample handling or with the equipment used.

Regardless of the analysis method used, it is important to have a good understanding of the limits of the measurement methods used, because, just like the location of sampling sites and the sampling frequency and period, the type of method used influences the interpretation of the results and the ability to make recommendations.

Before choosing the method of analysis, it is important to be familiar with certain technical concepts that can guide this choice. These concepts are summarized in the box

below and discussed in the sections below entitled *Simplified field analyses* and *Standard laboratory analyses*.

BASIC CONCEPTS RELATED TO THE RELIABILITY OF SAMPLE ANALYSIS METHODS

Method detection limit: the smallest detectable concentration of a parameter that gives a signal significantly different from the blank (distilled water).

<u>Limit of quantification</u>: the smallest value (concentration) of a parameter that can be quantified. This value is generally slightly higher than the detection limit. The product can be detected, but it may not be possible to determine its concentration level with precision.

<u>**Precision**</u>: closeness of agreement between results obtained by replicate measurements (n = 10 replicates) under controlled conditions. Precision can be expressed in different ways:

- <u>Replicability</u>: closeness of agreement between successive results obtained on the same sample tested in the same laboratory under the following conditions: same analyst, same equipment, same day.

- <u>Repeatability</u>: closeness of agreement between individual results obtained on a given sample tested in the same laboratory and for which at least one of the following is different: the analyst, the instrument, the day.

- <u>Reproducibility</u>: closeness of agreement between the individual results obtained on a given sample subjected to testing in different laboratories under the following conditions: different analyst, different instrument, different or same day.

<u>**Trueness**</u>: closeness of agreement between the average result that would be obtained by applying the experimental procedure 10 times (n = 10 replicates) and the certified value provided by a recognized organization. Trueness is measured, at a given concentration level, in the practical quantifiable zone of the method.

Adapted from the document *Protocol de validation d'une méthode d'analyse en chimie, Programme d'accréditation des laboratoires d'analyse (CEAEQ 2009).*

Simplified "field" analyses

There are a number of simplified methods for water quality analysis that can be used on site, thereby reducing the cost of each analysis. These simplified field methods often have much higher detection limits than laboratory methods. When a simplified method is selected, particularly for use over a long period, it is essential to establish the precision of the measurements, particularly if different kits are used at various locations by different users.

Since 2006, MDDEFP has made water quality monitoring kits available to watershed organizations. The kits contain a portable spectrophotometer, glassware, the necessary

solutions and chemical reagents for monitoring six parameters: suspended solids, apparent colour, ammonia nitrogen, nitrate, orthophosphate, and total phosphorus.

 Table 7 presents the methods used with the kit and their detection limits.

Parameter	Method *	Detection limit
Suspended	Method 8006	5 to 750 mg/L
solids	DOC316.53.01139	
	Photometric Method	
	Adapted from Sewage and Industrial Wastes, 31, 1159 (1959).	
Colour, true and	Method 8025	14 to 500 units
apparent	DOC316.53.01037	
	Platinum-Cobalt Standard Method	
	Adapted from Standard Methods for the Examination of Water and	
	Wastewater and NCASI, Technical Bulletin No. 253, December 1971.	
	Adapted from Wat. Res. Vol. 30, No. 11, pp. 2771–2775, 1996.	
Total nitrogen	Method 10071	0.5 to 25.0 mg/L N
	DOC316.53.001086	
	Persulfate Digestion Method	
Ammonia	Method 8155	0.01 to 0.50 mg/L NH ³ -
nitrogen	DOC316.53.01077	Ν
	Salicylate Method	
	Adapted from Clin. Chim. Acta., 14, 403 (1966)	
Nitrate	Method 8171	0.1 to 10.0 mg/L NO ³ -N
	DOC316.53.01069	
	Cadmium Reduction Method	
Nitrate	Method 8192	0.01 to 0.50 mg/L NO ³ -
	DOC316.53.01067	Ν
Tatal	Cadmium Reduction Method	
Total	Method 8190	0.06 to 3.50 mg/L PO ₄ ³⁻
phosphorus**	DOC316.53.01121	
	PhosVer® 3 with Acid Persulfate Digestion Method	0.02 to 1.10 mg/L P

 Table 7:
 Simplified methods for water quality monitoring

*Source: Hach analytical methods for the DR 2800 spectrophotometer.

http://www.hach.com/dr-2800-portable-spectrophotometer-with-lithium-ion-battery/product-parameter-

(Last accessed January 10, 2010).

** Conversion factor: PO₄-P = PO₄ / 3.07

The use of a simplified method can reduce the cost of measuring the various parameters. The above-mentioned kit costs roughly \$4,700 and can be used for approximately 100 analyses of each parameter before the chemicals need to be replenished. For subsequent sampling, the cost of these products for each parameter measured is approximately \$1 per sample. It takes approximately 1 hour per sample to measure all the selected parameters, if the user is well organized. However, users should not seek to reduce the costs if there is a risk of adversely affecting the reliability of the results. When using a simplified method, it is very important to know its limits and to validate its precision (by testing the same sample several times) and trueness (by comparing the results obtained with those of an accredited laboratory).

The results obtained with field kits are useful for conducting exploratory studies and identifying streams that may be problematic. However, their use for monitoring changes in

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water quality over time is not recommended. The level of precision of the methods cannot be determined because it depends on the user. Different users, who are not equally meticulous, could obtain very different analytical results if the work methods have not been standardized and controlled. In such cases, it is virtually impossible to distinguish between sources of variability in the results (intrinsic variability or variability associated with working methods).

In addition, with simplified field methods, the quantification limit is generally considered equivalent to the detection limit. The latter is generally higher than that of standard laboratory methods.

Standard laboratory analyses

In order to compare various streams and to conduct monitoring over time, it is important to ensure that the methods used are reliable and stable in time. There are many sources of error in water quality monitoring, including human error during sample collection and handling and equipment error (detection limits, calibration, wear). To be able to make findings and comparisons and provide recommendations, it is essential to minimize sources of error. The use of a standard analysis technique ensures stability between samples and projects and facilitates the interpretation of results.

CEAEQ provides standard analytical methods for monitoring a series of environmental quality indicators and standard sampling methods on its web site. We have reproduced the methods employed to measure the main parameters used in the monitoring of water quality in agricultural areas and their detection limits (Table 8Erreur! Source du renvoi introuvable.). For each analysis, CEAEQ provides information on the reliability of the methods used. This makes it possible to know the detection and quantification limits, and the precision and trueness of each analysis (Annex 2). When a laboratory is hired to analyze samples, it should be able to provide specific information on each of the characteristics required to determine the precision of an analysis.

For nitrates-nitrites, ammonia nitrogen, total phosphorus and suspended solids (filtration of 1 L of water), the quantification limit is 2 to 7 times lower than the IQBP criterion for good water quality. For example, for total phosphorus, the criterion for good water quality is 0.03 mg-P/L and the quantification limit is 0.006 mg-P/L, or 5 times lower. This discrepancy between the quantification limit and the most stringent quality criterion minimizes errors in the interpretation of results. However, for the concentration of suspended solids, if only 500 mL of water is filtered, it is not possible to determine whether the water is of good quality according to the IQBP criterion on the basis of the quantification limit. If only 500 mL of water is used, the quantification limit for SS is 9.94 mg/L. In order to be below the criterion of 6 mg/L used in the IQBP index (**Annex 2**) to classify water as being of good quality, the use of 1 L of water with a quantification limit of 3.5 mg/L is required.

Parameter	Standard method	Field of application
Suspended solids	Gravimetric method Centre d'expertise en analyse environnementale du Québec MA. 104 – S.S. 1.1 Published: 2008-04-11	Drinking water, surface water, groundwater and wastewater. Limit of quantification: With 500 mL of water: 9.94 mg/L for 1.2-µm filters and 13.7 mg/L for 0.45- µm filters With 1 L of water: 3.5 mg/L for filtrations with 1.2-µm filters
Fecal coliforms	Identification and counts of fecal coliforms (thermotolerant) and confirmation of <i>Escherichia coli</i> species: membrane filtration method CEAEQ MA. 700 – Fec.Ec 1.0 Published: 2003-12-05 Revised: 2005-12-15 (2)	Wastewater, groundwater, surface water and drinking water Limit of quantification: 20 and 60 CFUs of fecal coliforms
Total nitrogen	MA. 303 – N tot 1.0 Published: 2006-05-29 Revised: 2009-07-21 (2)	Drinking water, groundwater and surface water Limit of quantification: 0.07 mg/L N
Ammonia nitrogen	Automated colorimetric method with sodium salicylate CEAEQ MA. 303 – N 1.0 Published: 1999-02-10 Revised: 2009-07-21 (3)	Drinking water, groundwater and surface water Limit of quantification: 0.07 mg/L NO3- NO2-N
Nitrates and nitrites	Automated colorimetric method with hydrazine sulphate and N-(1-Naphthyl)ethylenediamine dihydrochloride CEAEQ MA. 303 – NO3 1.1 Published: 2009-07-14	Drinking water, groundwater and surface water Limit of quantification: 0.07 mg/L NO3- NO2-N
Total phosphorus	Determination of total phosphorus in natural waters: mineralization by persulphate; automated colorimetric method; procedures adapted to phosphorus at low concentrations and trace levels CEAEQ MA. 303 – P 5.0 Published: 2003-10-08 Revised: 2010-03-09 (4)	Natural waters Limit of quantification: 0.006 mg/L P

 Table 8:
 Standard analytical methods for water quality monitoring

Source: Analytical methods. Centre d'expertise en analyse environnementale du Québec (CEAEQ). http://www.ceaeq.gouv.qc.ca/methodes/chimie_inorg.htm

1.2.4 PRESENTATION AND INTERPRETATION OF RESULTS

Ideally, the monitoring data should be compiled in an easily searchable database. For example, the U.S. EPA has a water quality data compilation service called STORET. Environment Canada has developed a management tool called ENVIRODAT; however, few data are currently available online.¹¹ There is no equivalent service in Quebec.¹² If data compilation software is unavailable, the use of a spreadsheet or database software should permit effective analysis of the data.

A file should always be created at the outset for storing raw (unanalyzed) data. The file should be as simple as possible so that it can be subsequently transferred to any database. The GPS coordinates of the sampling sites could be entered when recorded. This file should also contain basic information on the sampling method, the date and time of collection, the water level (see section 3.1), and the analytical methods used for each parameter. The data can then be recorded or transferred to another file for analysis.

Representation of raw data

Before conducting statistical analyses, it is important to obtain an overall picture of the information collected. This overall picture should then be systematically presented in the dissemination of the results. Graphical representations of raw data (see example in **Figure 1**) make it easier to visualize and understand the data. With this type of representation, the user can grasp the following information at a glance:

- the parameters monitored
- the sampling period
- the sampling rate
- the number of samples
- the variation in the parameters over time
- extreme values
- presence of a discernible trend
- variations in concentrations of each parameter in relation to basic quality criteria
- variations in concentration of each parameter based on water level¹³

¹¹ <u>http://www.ec.gc.ca/eaudouce-freshwater/default.asp?lang=Fr&n=EFDA57C6-1</u>

⁽last accessed April 11, 2012).

¹² Water analysis results of projects carried out in collaboration with MDDEFP can be compiled in the MDDEFP aquatic environment quality monitoring database (BQMA).

¹³ The hydrologic regime has a significant impact on nonpoint source pollutant loads. It is crucial to present data related to water levels and rainfall (see Section 3).

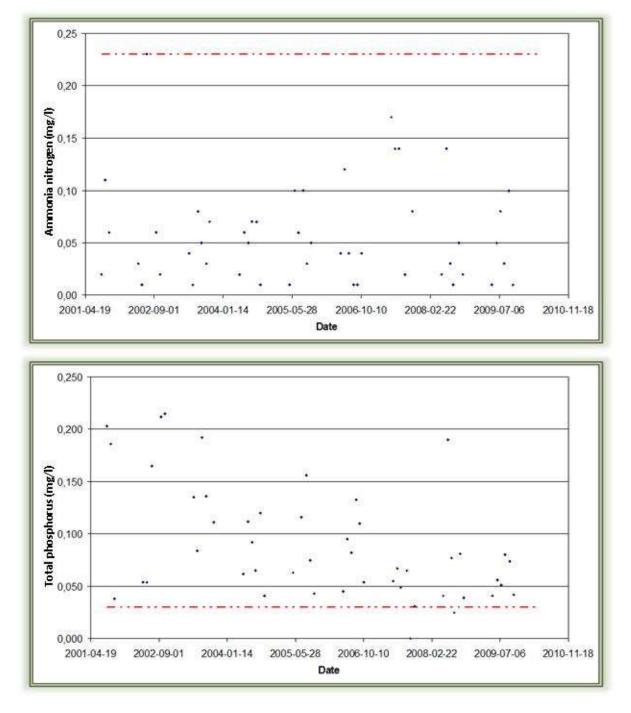


Figure 1: Sample graph of ammonia nitrogen and phosphorus concentrations in a river (the dotted red line indicates the criteria for high quality water)

Analysis of results

Although the raw data provide significant information and an overall picture, their interpretation generally requires a more detailed treatment. The use of statistical analyses is essential, especially if the data are needed to compare streams, identify water quality trends, or calculate the pollutant load transported by a stream.

The figure above (**Figure 1**), presenting the raw data collected, provides a sufficient indication of water quality from the standpoint of phosphorus and ammonia nitrogen. It can be seen that all the samples contain concentrations below the threshold value for ammonia nitrogen and above the threshold value for phosphorus. The results seem to be clear-cut. However, the use of statistical analyses can permit a better understanding of this seemingly obvious information. This is especially true in situations involving both positive and negative deviations. **Table 9** shows an example of the application of statistical calculations to the data in **Figure 1** and shows how these calculations can permit a more in-depth analysis.

Table 9: Statistical representation of data in Figure 1 (phosphorus only)

	Threshold value*	Min.	Q 25	Median	Q 75	Max.
TOTP (mg/L)	0.030	0.025	0.054	0.077	0.077	0.133

*: Class A of the IQBP. Number of samples analyzed: 15

Note: Calculation of the median value of the samples (0.077) makes it possible to determine the magnitude of the deviation (and therefore the remedial action required) from the threshold value (0.030) beyond which the water body can be considered contaminated. Note that the median is preferred over the mean because it can mitigate the influence of extremely low (0.025) and high (0.0133) values. The IQBP is calculated using the median values. The first quartile (0.054) and the third quartile (0.077) show that an effort should be made to determine whether the deviations between these groups of samples are significant and can be explained by such factors as rainfall, the sampling location or the growing season.

In Section 3 of this document, which focuses on hydrologic indicators such as flow, water level and rainfall, we will further illustrate the use of statistical calculations of this type. Measuring hydrologic indicators is essential for drawing reliable conclusions from a comparison of streams, including the load transported by the streams, or for identifying significant trends in the improvement of stream water quality, especially over a short period of time (3-5 years).

SECTION 2 BIOLOGICAL INDICATORS OF WATER QUALITY

2.1 DEFINITION OF BIOLOGICAL INDICATORS

Physicochemical and bacteriological indicators reflect changes in water composition. Other types of indicators also exist that provide information on the response of aquatic ecosystems to physicochemical changes in the water, i.e., biological indicators. **Biological indicators can be used to assess the presence, absence, number or varieties of plant or animal organisms present in a body of water.**

A number of biological indicators exist. The two main indicators used by MDDEFP in Quebec are the Standardized Global Biological Index (IBGN) and the Biotic Integrity Index (IIB).¹⁴ The IBGN is based on the analysis of benthic macro-invertebrates (insects, worms, molluscs, etc.); it *provides a synthesis of the overall quality of the environment*.¹⁵ The IIB is based on the analysis of fish communities. It is used to determine whether a stream *supports and maintains a balanced, well integrated community of organisms capable of adapting to change and having a species composition, diversity and functional organization comparable to those of a natural ecosystem.*¹⁶

These indices reflect both water quality and the state of the aquatic environment. In other words, in addition to the physicochemical and bacteriological state of the water, these biological indicators are sensitive to habitat quality, i.e., to the characteristics of the stream itself (water level during low flow periods, the condition of stream banks and shorelines, presence or absence of shade, presence of pools, riffles, etc.). They provide a good indication of the state of a stream, because they reflect the cumulative impact of a series of deterioration factors. Those interested in conducting this type of monitoring can obtain more information on the MDDEFP site.¹⁷

However, biological indicators are of little use for assessing the impacts of nonpoint source pollution, because they cannot distinguish between the importance of water composition and the state of the habitats.

¹⁴ Biological communities are good indicators of ecological integrity. They integrate the characteristics of their habitat, in space and time, and respond to the many physical and chemical disruptors of aquatic ecosystems, allowing for the assessment of their cumulative and synergistic past and present effects on ecosystems. The use of various aquatic organisms makes it possible to integrate various spatial/temporal scales due to the variable life cycle, physiology and mobility of the organisms.

¹⁵ <u>http://www.mddep.gouv.qc.ca/eau/sys-image/glossaire2.htm</u> (last accessed July 21, 2010)

¹⁶ Ibid.

¹⁷ <u>http://www.mddep.gouv.qc.ca/eau/flrivlac/criteres.htm</u> (last accessed July 21, 2010)

Guidelines for Surface Water Quality Monitoring in Small Agricultural Watersheds

Eastern Canadian Diatom Index

For water quality monitoring associated with nonpoint source pollution in agricultural watersheds, there is one biological indicator, the Eastern Canadian Diatom Index, that appears to be particularly useful. The classification of diatoms, a group of algae, makes it possible to link the presence of various species to the state of eutrophication of a stream and, indirectly, to the concentrations of phosphorus and nitrogen. Research on diatoms indicates that, unlike the previously described indicators, their development is *not highly influenced by stream size or by habitat* (Campeau 2009). However, diatoms are particularly sensitive to the presence of phosphorus, nitrogen and organic matter in water. They are also affected by pesticides, pH and conductivity.

Over 500 diatom species have been identified in Eastern Canada, some of which are more sensitive to pollution than others. Researchers at the Université du Québec à Trois-Rivières have developed an index, based on the analysis of 200 diatom species, which divides streams into five classes:

- A: Oligotrophic environment (non-eutrophic);
- B: Oligo-mesotrophic environment;
- C: Mesotrophic environment;
- D: Meso-eutrophic environment;
- E: Eutrophic environment

The diatom species present in Class A streams are the most sensitive to pollution. They will therefore be found in larger numbers in unpolluted streams, and will gradually disappear as stream pollution increases. Conversely, polluted streams (Class C and D) contain a higher proportion of more pollution-tolerant diatom species.

The index that was developed is known as the Eastern Canadian Diatom Index (IDEC) (Campeau et al. 2009) and can be used to assess the degree of eutrophication of a stream on the basis of the proportion of pollution-sensitive or pollution-tolerant diatom species present in it. **Table 10** presents the IDEC for alkaline streams. ¹⁸

¹⁸ Note: Diatom species are very sensitive to stream acidity. IDEC is divided into three sub-categories: IDEC-neutral for streams whose natural pH (i.e., unpolluted state) should be neutral; IDEC-alkaline; and since 2010, a third class corresponding to watersheds rich in carbonate rock, whose streams have a high pH (Lavoie et al. 2010). In Quebec, IDEC-neutral is generally be used for streams on the Canadian Shield; IDEC-alkaline for streams in the Appalachians and the St. Lawrence Plain; and IDEC-carbonate for certain streams located primarily in the St. Lawrence lowlands. The pH is measured systematically during sampling.

Table 10: Interpretation of IDEC (alkaline classes)

Ecological status	IDEC	Rank	Interpretation	Classes of several Quebec streams between 2002 and 2003 U (upstream) – D (downstream)
Reference	81-100	A	Oligotrophic	Chaudière (U)
			The diatom community corresponds to reference (undisturbed) conditions. It is the community typical of alkaline conditions. Little or no human-induced alteration has occurred. Total phosphorus concentrations are less	Yamaska Sud-Est (U)
			than 0.03 mg/L and organic and mineral loadings are very low in the weeks preceding sampling. This is called an oligotrophic stream.	Trout River (U)
Good	61-80	В	Oligo-mesotrophic	Magog (D)
			There are slight changes in the composition and abundance of diatom species relative to reference communities. These changes indicate low levels of human-	Massawippi (D)
			induced alteration. Nutrient concentrations and organic and mineral loads are low in the weeks preceding sampling. This is called an oligo-mesotrophic stream.	Yamaska (U)
Moderate	41-60	С	Mesotrophic	Coaticook (D)
			The composition of the diatom community is moderately different from that of the reference community and is significantly more disturbed than communities in good condition. The values show moderate signs of human-induced alteration. There are episodes of high nutrient concentrations and/or organic and mineral loadings in the weeks preceding sampling. This is called a mesotrophic stream.	Des Anglais (U) Chaudière (D)
Poor	21-40	D	Meso-eutrophic	Chateauguay (D)
			The diatom community is severely altered by human activity. Species sensitive to pollution are absent. There were, in the preceding weeks, frequent episodes where	Richelieu (D)
			nutrient concentrations and/or organic and mineral loadings were high. This is called a meso-eutrophic stream.	Yamaska Sud-Est (D)
Very poor	0-20	Е	Eutrophic	Bayonne (D)
			This diatom community is among the most degraded in the rivers of Eastern Canada. It is severely affected by human activity. It is composed exclusively of species that are	Yamaska (D)
			highly tolerant of pollution. Nutrient concentrations and/or organic and mineral loadings are constantly high in the weeks preceding sampling. This is called a eutrophic stream.	Des Hurons (D)

Source: Lavoie et al. 2006, Grenier et al. 2006 in Campeau, S., Prévost, I. and Rousseau Beaumier, T., 2010. Suivi de 50 cours d'eau à l'aide de l'indice IDEC dans le cadre des Projets collectifs agricoles (PCA). Report presented to the Quebec Department of Sustainable Development, Environment and Parks as part of the Projets collectifs agricoles (PCA). Université du Québec à Trois-Rivières, March 2010, 16 p

The diatom species present at the time of sampling reflect the state of the aquatic environment (variations in organic loads and nutrient concentrations) in the weeks preceding sampling (approximately five weeks).

The monitoring of diatoms involves simple, quick and relatively inexpensive procedures. However, the diatom index cannot be used to identify the particular parameter responsible for eutrophication, although in freshwater, in Quebec, phosphorus is more often responsible for accelerated eutrophication than nitrogen.

2.2.1 DIATOM SAMPLING STRATEGY

The sampling of diatoms is very simple, which explains the interest in it. It requires the collection of one or two samples between July and September.

Researchers recommend that **monitoring be done over a period of at least three years** in order to take into account of interannual variations before the state of the stream is assessed. Samples are **collected at the sites where the state of stream eutrophication is to be measured.** The downstream portion of the watershed in question is generally a good location as it receives all water flowing into the watershed.¹⁹

Sample collection

The basic rules of sampling are outlined below.

Select a sampling site, preferably a fast-flowing section of the stream in a sunny location.

If there is a bridge or dam, select a site upstream from the bridge and downstream from the dam.

Identify sources of point source discharges and collect samples upstream from these discharges.

Collect samples on a rocky substrate. If there are no rocks in the stream, rocks can be placed in the stream one month prior to sampling.

Avoid sampling the week following heavy rainfall. If the water level of a stream is too high, rocks cannot be collected from the bottom and it is therefore possible that rocks that were not covered by water several days previously will be sampled, which will distort the results.

Sampling procedure

Using a toothbrush, scrape the algae from the surface of five rocks spaced no more than 50 m apart and at a depth of 20 to 60 cm (depending on the transparency of the water). The rocks must be submerged during the low flow period (in the weeks preceding sampling). They must not be covered with long filamentous algae.

Place the algae in a container with a small amount of stream water. Thoroughly clean and rinse the toothbrush between samplings to avoid contamination.

Add Lugol's (potassium iodide) solution, and store the samples in the dark at 4°C until they are analyzed.

¹⁹ The watershed research laboratory of the Université du Québec à Trois-Rivières can be contracted for specific up-todate information on sampling. The laboratory can also provide support for the sampling strategy.

2.2.2 ANALYSIS OF SAMPLES AND INTERPRETATION OF RESULTS

Although a diatom identification guide does exist,²⁰ diatom identification and counts require a high level of expertise. The watershed research laboratory of the Université du Québec à Trois-Rivières provides analytical services at a cost of approximately \$250 per sample (price in the summer of 2010). Diatom monitoring results are interpreted on the basis of the calculation of the IDEC. For a better assessment of the results, the IDEC classification should always be accompanied by the raw diatom count data.

The designation of a stream as Class D indicates that it should be given priority in restoration efforts. Stream restoration efforts should seek to bring the stream up to Class B, although moving a stream from Class D to Class C and keeping it there for several years would be an important first success in terms of restoration.

²⁰ Lavoie, I., P.B. Hamilton, S. Campeau, M. Grenier and P.J. Dillon, 2008.

Guide d'identification des diatomées des rivières de l'Est du Canada. Presses de l'Université du Québec, 241 pages and 68 taxonomic plates (ISBN 978-2-7605-1557-4).

SECTION 3 HYDROLOGIC MONITORING INDICATORS: RAINFALL, WATER LEVEL AND FLOW

Some water quality measurement indicators can be described as indirect. While they do not rank actual water quality, the information they provide is critical for correctly assessing water quality results, primarily with regard to physicochemical and bacteriological contaminants. Indirect indicators can and, in many cases must, be included in a water quality monitoring protocol.

The water flowing in a stream comes from surface runoff, interflow (shallow lateral subsurface flow above the water table) and groundwater discharge. Precipitation that falls directly onto water bodies is considered a small component of streamflow. Except during high flow periods or heavy rains, the water level of a stream generally corresponds to the upper level of the groundwater aquifer.²¹ The stream is thus fed only by subsurface flows. During heavy rainfall, part of the water flows across the surface as runoff and enters streams without infiltrating into the subsurface. This portion of runoff generally represents 30 to 50% of total precipitation during snowmelt or when the soil is saturated.

While the primary source of point source pollution is pollutant loads in wastewater discharges, nonpoint source pollution is primarily influenced by intensive hydrologic events, i.e., snowmelt and rain events. When it rains little or not at all, pollutants remain in place or gradually seep into the soil. The physical characteristics of the pollutant and the duration and intensity of rainfall determine the extent to which it infiltrates (leaches) into the soil as well as its surface transport (runoff) to streams. Variations in the hydrologic regime have a major influence on nonpoint source pollutant loadings and on the concentration of the various physicochemical and bacteriological parameters in the water.

There are three indicators that can be used to obtain a more or less detailed picture of the hydrologic regime:

- 1. rainfall duration and intensity and the period between rainfall events (pluviometry);
- 2. stream water level (stage or height of the water at a constant fixed point);
- 3. discharge (volume in cubic metres or litres) per selected unit of time (seconds or hours) through a predetermined point.

Depending on the objectives of the monitoring protocol, the measurement of one or more of these indicators may be necessary to ensure the representativeness of the water quality monitoring samples and accurate interpretation of the results and to calculate the pollutant load transported by a stream.

²¹ Some water tables may be located at much greater depths and may never be in contact with the atmosphere.

3.2 IMPORTANCE OF MEASUREMENTS OF THE HYDROLOGIC REGIME

The monitoring of one or more hydrologic regime indicators is particularly important in many water quality monitoring protocols. Knowledge of the hydrologic regime is often essential for ensuring sample reliability and an accurate interpretation of the results. For monitoring protocols based on the measurement of the pollutant load of a stream, knowledge of the hydrologic regime is critical.

3.2.1 ENSURING THE REPRESENTATIVENESS OF SAMPLES AND CORRECT INTERPRETATION OF THE RESULTS

Information on the hydrologic regime is used to determine the state of the stream during sampling (low flows, high flows, receding flows, baseflow, etc.). It is also used to situate the sampling dates relative to an entire season (dry period, period of heavy rainfall, etc.). This information, gathered at the time of sampling, is critical to the interpretation of water quality results.

The interpretation of a water quality result generally requires an analysis of variations in the concentration of a physicochemical parameter in the water (e.g., phosphorus). However, this analysis is inadequate if no relationship has been established between the variations in concentrations and streamflow. As mentioned above, during dry periods, there is little or no transport of nonpoint source pollutants to streams. A water quality result showing a decline in pollutant concentrations during low flows would be meaningless in terms of the control of nonpoint source pollution. In order to conclude that there has been an improvement in water quality, a decline in the concentrations of a given pollutant must be observed when flows correspond to periods of sufficiently heavy rain to cause runoff. Therefore, without monitoring flows, it is difficult to establish trends.

In order to be able to detect changes in water quality over time and to determine whether the changes are associated with particular seasons or particular flow conditions, the concentration vs. flow relationship must be defined and statistical analyses must be performed (Hirsch et al. 2010).

As an example of the importance of defining the relationship between the concentration of a particular parameter and flow, **Figure 2** illustrates the decline in phosphorus concentrations between a reference period (1979 to 1995) and the period during which changes were made to the watershed (1995-2004). The concentration vs. flow relationship shows that there is a significant reduction in the concentration of phosphorus when the sample is collected under low flow conditions (flow less than 100 m³/h), whereas it is virtually non-existent when collected at high flows (4,000 m³/h).

In this specific case, the specialists' interpretation is that the reduction in concentrations during low flows is associated with remediation efforts aimed at reducing point sources of pollutants. During low flows, point sources are the primary sources of pollutants and nutrients to the river. They also conclude that nonpoint source loadings remain abundant because when the flow increases (rainfall promoting leaching or runoff),

phosphorus concentrations increase and that there is no difference between the period selected as the reference period and the period used for the analysis during high flows.

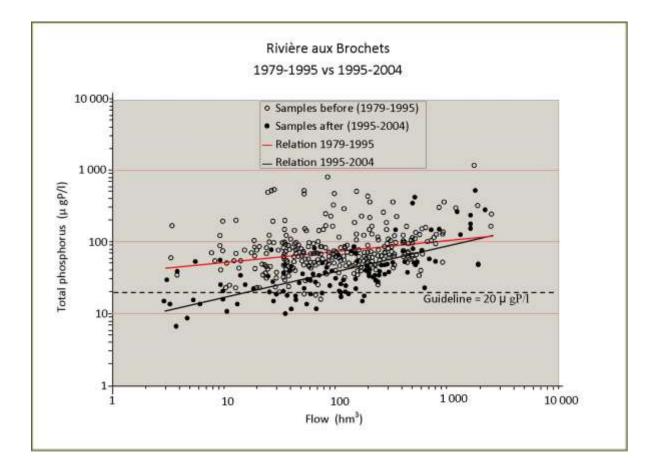


Figure 2: Changes in phosphorus concentrations in Rivière aux Brochets as a function of flow Source: Adapted from Simoneau, M. 2007. État de l'écosystème aquatique du bassin versant de la baie Missisquoi: faits saillants 2001-2004, Québec, ministère du Développement durable, de l'Environnement et des Parcs, direction du suivi de l'état de l'environnement, ISBN 978-2-550-49625-0 (PDF), 18 p.

3.2.2 LOAD ASSESSMENT

Monitoring of the hydrologic regime is also critical to calculating the pollutant load of a stream, and thus measuring the contribution of that stream to the deterioration of a body of water. By measuring pollutant loads, it is also possible to establish reduction objectives for each stream draining into a body of water and to quantify the impact of pollution control measures (e.g., implementation of good agricultural practices).

A load is the quantity of a physicochemical parameter entering a stream during a given period of time (day, month, year) and is generally expressed in kilograms or tonnes. In agricultural watersheds, loads of phosphorus, total nitrogen and suspended solids are generally calculated. Loads are calculated by multiplying the concentration (mg/L or kg/m³) of the selected parameter by streamflow (m³/y). If the objective is to determine the load transported by the stream, it is critical to measure flow.

Care must be exercised in the interpretation of the results of load calculations in several respects. First, the load of a stream is influenced by the concentration of the parameter studied, but even more so by the intensity of precipitation and therefore the volume of water transported. This means that a drier year could result in a reduction in stream loadings, and a wet year in an increase in loadings. In the analysis of the load transported, the volumes of water transported and the amount and distribution of precipitation received during the year must always be indicated.

The contribution of an area can be calculated in terms of daily or annual load (in kilograms per day (kg/d) or tonnes per year (T/y), but also in terms of export rates (kg/ha or kg/km²) over a given period. It is important to distinguish between the two ways of presenting the information. In the first case, the area of the drainage basin is not taken into account and it is therefore more difficult to ascribe meaning to the load data. It is normal that the pollutant load of a larger watershed be greater than that of a smaller watershed. Thus, without any information on area, it is impossible to draw comparisons between watersheds.

The relative contributions of different watersheds to pollutant loading can be classified based on their rates of export. This makes it possible to target areas in which it may be easier to achieve load reductions (based on the principle that it is easier to reduce surplus loads than to eliminate the final few kilograms) or zones in which it is important to limit the increase in exports so as to compensate for areas with surplus loads.

Threshold values for determining acceptable loads

There are no generally recognized threshold values for assessing what constitutes an acceptable or unacceptable export load for the surface area of a given watershed. However, for some bodies of water, the responsible authorities have developed objectives to be achieved in order to protect or restore certain water uses.

Under the U.S. *Clean Water Act,* states are required to prepare a list of bodies of water that do not meet the water quality standards. These states must then define the total maximum daily load (TMDL), which is the maximum amount of a pollutant that a body of water can receive daily while still meeting quality standards. TMDLs are actually usually presented in the form of kilograms per year. The U.S. Environmental Protection Agency

web site provides examples of load estimates of nitrogen, phosphorus and suspended solids for certain streams in the United States.²²

In Quebec, a target for the reduction of phosphorus loading has been set for Missisquoi Bay (128,200-ha watershed). The phosphorus load (2002-2005 average) of streams draining Quebec watersheds towards Missisquoi Bay is 69 T/y (or 0.54 kg/ha/y) (Smeltzer and Simoneau 2008). Under the Quebec-Vermont agreement signed in 2002, the target phosphorus load to be reached in 2016 is 38.9 T/y (or 0.30 kg/ha/y), a 41 to 43% reduction from the anticipated load in Quebec. Such a reduction (combined with that required for Vermont) would make it possible to reach a total phosphorus concentration of 25 μ g/L in the Bay, which would limit the rate of eutrophication of the Bay.

At another scale, in 2005, MDDEFP released a study of the maximum loads that should not be exceeded in the major rivers of Quebec to prevent their eutrophication and that of their outlets (Gangbazo et al. 2005). By comparing this reference load with the actual estimated load, the authors were able to determine the necessary remediation efforts. For example, the phosphorus load transported by the Yamaska River (451,000-ha watershed) is reported to be 310 T/y (or 0.69 kg/ha/y) and the target load is 65 T/y (0.14 kg/ha/y), which translates into a reduction target of 245 T/y (0.54 kg/ha/y).

Apart from these cases, which are currently rather exceptional in Quebec, there are no absolute classes defined by the various levels of government that establish the loadings or export rates per hectare considered acceptable or excessive in a given watershed or in a given ecological area. However, the establishment of pollutant export rates per hectare can make it possible to compare sub-watersheds (within a larger watershed) and to identify those that have the highest export rates.

Table 11 presents the total phosphorus export levels reported in the literature according to the type of land use. The first series of data comes from a scientific article that presents, in the references, average export levels according to land use (Dorioz et al. 2001). The second and third series come from studies on phosphorus monitoring in Missisquoi Bay (Smeltzer and Simoneau 2008; Michaud et al. 2005), which present the export rates for various streams emptying into the Bay. The last series of data is taken from the previously mentioned study by Gangbazo et al. (2005).

²² <u>http://water.epa.gov/lawsregs/lawsguidance/cwa/tmdl/</u> (last accessed November 28, 2011). Note that the FLUX software (see below) is generally used to establish annual loads, which are calculated using curves of the relationship between the pollutant concentration and the average daily flow.

Table 11:	Examples of phosphorus export rates per hectare per year
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Watersheds and land use		Export rate(kg P/ha/y)
Extensive forestry and agricult	ural watersheds	0.04 to 0.2
Agricultural watersheds	Hay fields	0.4 to 1.1
	Pasture	0.1 to 0.8
	Crops	0.7 to 2.5
Urban watersheds	Residential	0.5 to 1.5
	Industrial	1.2 to 2.5

Source: Adapted from Dorioz et al. 2001

Watersheds and land use	Export rate (kg P/ha/y)
Sutton (Missisquoi Bay watershed) (2002-2005)	0.55
Brochets (Missisquoi Bay watershed) (2002-2005)	0.66
Ewing (Missisquoi Bay watershed) (2002-2005)	1.20
Ruisseau au Castor (Missisquoi Bay watershed) (2002- 2005)	1.55

Source: Adapted from Smeltzer and Simoneau 2008

Watersheds and land use	Export rate (kg P/ha/y)
Ruisseau au Castor 1997-1998	1.4
Ruisseau au Castor 1998-1999	0.63
Ruisseau au Castor 2001-2002	1.29
Ruisseau au Castor 2002-2003	1.41

Source: Adapted from Michaud et al. 2005

Watersheds and land use	Export rate (kg P/ha/y)
Boyer	1.05
Chaudière	0.21
Saint-François	0.41
Yamaska	0.65

Source: Adapted from Gangbazo et al. 2005.

In 2006, the Alberta Ministry of Environment and Water published a literature review on export coefficients for total phosphorus, total nitrogen and total suspended solids (Alberta Environment 2006). The main findings of that review are outlined below.

Land use	Total phosphorus (kg/ha/y)	Total nitrogen (kg/ha/y)	Suspended solids (kg//ha/y)*
Unmanaged forests	0.01 to 0.2	0.5 to 2.5	250
Managed forests	0.2 to 0.8		
Grasslands and pastures	0.3 to 1.0	1.0 to 5.0	400 to 500*
Other crops (variable)	0.5 to 5.0	2.0 to 15.0	1,500 to 5,000

Table 12: Examples of export rates

Source: Adapted from Alberta Environment (2006).

*For suspended solids, few studies have been identified, with only two to three studies per category.

As previously mentioned, hydrologic regime monitoring was conducted using three indicators: precipitation duration and intensity,²³ stream water level and flow. The information provided by each indicator and the costs of monitoring will vary depending on the rate and precision of the measurements that are carried out. There are three possible levels of precision in the measurement of the hydrologic indicators, ranging from the simplest to the most complex:

- Basic level: The monitoring of total daily precipitation and water level during sampling without flow measurement;
- Intermediate level: The continuous monitoring of precipitation and water level without flow measurement;²⁴
- Advanced level: Continuous monitoring of precipitation, water level and flow.

The appropriate hydrologic indicator(s) must be selected in accordance with the objectives sought and the resources available and in such a way as to achieve maximum efficiency, with the level of precision adapted to the monitoring of the water in question. The costs of the monitoring protocol and the quality of the information obtained increase as a function of precision. However, it is not essential to seek the maximum level of precision for all protocols. For some protocols, a lower level of precision can be entirely sufficient, as will be illustrated below.

In the case of the calculation of the pollutant load transported by a stream, hydrologic monitoring requires advanced monitoring of the hydrologic regime, but also involves a series of adaptations and technical features that will be detailed in Annex 3 of this document.

3.3.1 BASIC LEVEL: MONITORING OF DAILY TOTAL PRECIPITATION AND WATER LEVEL DURING SAMPLING WITHOUT FLOW MEASUREMENT

The basic information that is required in order to be able to interpret the water quality monitoring results is daily precipitation, as provided by the weather station closest to the sampling site (rainfall height in mm per 24 h) for the entire duration of monitoring. This information is available on the Environment Canada web site.²⁵

²³ The analysis of rainfall results can cover the period between rainfall events, maximum intensity, average intensity, quantity (mm), etc.

²⁴ Water level measurements cannot be used to estimate the flow of a stream. A doubling of the height of the stream rarely corresponds to a doubling of flow due to the variable cross-section.

²⁵ http://climat.meteo.gc.ca/advanceSearch/searchHistoricData_f.html?timeframe=1&Prov=XX&StationID=9999&Year=20 10&Month=8&Day=25 (last accessed August 26, 2010).

This information should be accompanied by systematic measurement of water levels during sampling (following basic rules for this measurement - *see box*). The measurement of water levels during sampling must provide information on the state of the stream (low flow, high flow, etc.). The representativeness of the samples collected during the monitoring period can be assessed on the basis of an analysis of water levels and rainfall.

A FEW GUIDELINES FOR MEASURING WATER LEVEL:

- Always take the measurement from a fixed point at the same location. In small agricultural streams, the section selected for measurement can sometimes be unstable, resulting in distortion of the measurement data. It is therefore important to ensure that at that location, the section of stream does not change (no shoreline erosion, no deepening of the streambed, site not exposed to flooding by the downstream body of water).
- Record the exact location where the measurements are taken so that it can be easily found again for subsequent monitoring.
- If the monitoring is to be carried out over the long term, a staff gauge, which costs approximately \$65, can be installed in the stream (near a bridge or culvert). When the gauge is securely placed in a stable section of the stream, recording of water height is easy and stable over time.

It is important to bear in mind that the information obtained through rainfall and water level monitoring conducted in accordance with the above procedures provides only an approximate picture of the actual situation. If the watershed is very small, localized rainfall may not be recorded by the closest weather station. In addition, daily precipitation data do not provide specific information about precipitation intensity and duration. It is therefore very difficult to know how the watershed in question responds to rainfall without on-site observations and measurements. In small watersheds, if rainfall is intense, only a few hours may elapse between the rainfall event and the increase in water level. Similarly, the water level may drop back down again very quickly. It is therefore difficult to obtain a clear idea of the extent of runoff (principal mechanism of transport of nonpoint source pollution).

Although imperfect, such hydrologic regime monitoring should always accompany the water quality results obtained with lower-cost, basic level monitoring.

3.3.2 INTERMEDIATE LEVEL: CONTINUOUS RAINFALL AND WATER LEVEL MONITORING WITHOUT FLOW MEASUREMENT

Continuous rainfall and water level monitoring can be conducted in a relatively simple and economical manner, without the need to measure streamflow, which involves more complex and more costly procedures.

Such monitoring requires the installation of measurement systems near sampling points. A tipping bucket rain gauge combined with a clock and an electronic system can be used to measure the volume and intensity of all rainfall events. An automatic water level recorder can be employed to measure the water level of a stream using a predetermined time step. The combination of information provided by the two instruments will provide an overall picture of stream dynamics, depending on the intensity of rainfall, in contrast with the static picture provided by daily rainfall monitoring and discrete water level measurements.

The equipment required for such monitoring can be obtained for approximately \$2,500 per stream. This intermediate level provides more precise information on stream water level variations in time as a function of rainfall intensity and makes it possible to analyze the response of the watershed. To be useful, the collected rainfall data must be analyzed using a small time step (mm/hour) and must make it possible to distinguish different rainfall events. This is particularly important if the watershed under study is small and if the changes in water level occur rapidly. The objective of the rainfall analysis should be to determine whether the samples for the water analysis were collected from a stream that receives surface runoff (e.g., after heavy rain) or from a stream that is recharged exclusively from water that infiltrated into the soil.

When the objective of the monitoring is not to calculate transported loads but rather to obtain a more precise idea of the dynamics of concentrations (nitrogen, phosphorus, suspended solids) based on rainfall and runoff, intermediate level monitoring can be carried out at a lower cost than advanced monitoring, which includes measurement of streamflow.

3.3.3 ADVANCED LEVEL: CONTINUOUS MONITORING OF RAINFALL, WATER LEVEL AND FLOW

Advanced hydrologic regime monitoring combines continuous measurements of rainfall (see Section 3.3.2) and flow. Continuous monitoring of flow requires a higher level of knowledge and technical resources and is more costly and time consuming. It is carried out when the objective of water quality monitoring is to assess the contribution of a watershed or the impact of restoration practices.

Streamflow, or discharge, i.e., the volume of water (generally expressed in cubic metres or litres) that flows past a designated point over a fixed period of time (generally expressed in seconds or hours) is represented by a hydrograph (flow evolution over time - see **Figure 3**).

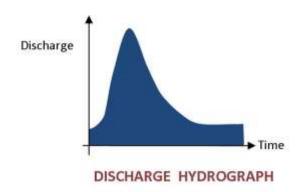


Figure 3: Discharge hydrograph Source: Musy (2005)

While various methods can be used to obtain a hydrograph, it is necessary to ensure continuous measurement of water level in a precalibrated structure, or continuous measurement of water level combined with either discrete flow measurements or continuous velocity measurement. **Table 13** presents various techniques and the associated measurement devices.

Method used to obtain hydrograph	Measured parameters	Devices used	Results	Comments
Continuous water level measurement in a pre- calibrated structure	Continuous water level	Pre-calibrated structure (weirs, flumes, etc.) Ultrasound probe Pressure probe, etc.	Discharge is calculated by entering the water level in a predefined equation for each structure.	These structures are well adapted to places where it is difficult to measure water velocity or in small watersheds where the flow changes very rapidly.
Continuous water level measurement without a pre- calibrated structure	Continuous water level	Ultrasound probe Pressure probe, etc.	Stage hydrograph (fig. 3).	The water level measurement must be taken in a stable section of the stream. ^a
+			Water velocity measured at different points in the stream is	
Discrete water velocity measurement	Water velocity and cross- section	Current meters: - universal current meters - Doppler current meters - electromagnetic probes, etc Graduated rod and tape for the cross-sectional area	combined with the cross-sectional area to obtain discrete measurements of discharge (Fig. 5). The discharge measurements are then combined with the water level to establish a rating curve (Fig. 4)	The number of verticals for the measurement of water velocity must be sufficiently large to clearly represent the entire profile.
or	Dye or salt dilution for discrete measurements	Tracers: salt, dye (e.g., fluorescein). Measurement tool: - conductivity meter - fluorimeter	Discharge is calculated using equations that take into account the dilution of the tracer in the stream. Discharge is combined with the water level to establish a rating curve (Fig. 4)	The use of salt as a tracer provides an inexpensive technique that is well suited to turbulent streams.
Continuous water velocity measurement in a defined structure	Continuous water velocity and water level in a structure with a stable cross-section (e.g., culvert)	Ultrasound probe, etc.	The continuous flow is calculated using an equation combining the water velocity and the cross- sectional area established for each water level measured.	These devices are generally more expensive

Table 13:Summary of techniques commonly used to measure flow

Source: Adapted from Musy (2005). ^a Water level can vary if the shoreline widens or narrows. It is therefore important to use fixed points (geodetic monuments, post, bridge, etc.) outside the stream as temporal reference points to ensure the stability of the shorelines.

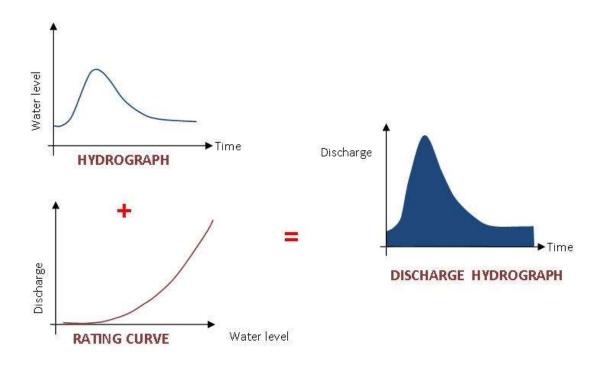


Figure 4: Converting a stage hydrograph to a discharge hydrograph using a rating curve (Source: Adapted from Musy (2005)

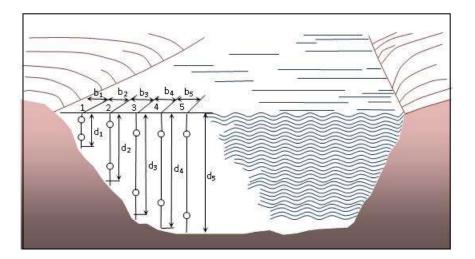


Figure 5: View of a stream cross-section showing the location of points for measurement of velocity. Velocity measurements are taken at the circles (Source: WMO 1994)

In practice, the level of overall uncertainty considered acceptable in the field of hydrology and agricultural pollution control, given proven techniques, is 15 to 20% (Benoist et al. 2002). An overly approximative method would give such a high level of uncertainty that it would be virtually impossible to interpret the results obtained.²⁶

²⁶ There are several manuals available online that provide procedures for the reliable measurement of flow, a few of which are listed below:

⁻ The Centre d'expertise en analyse environnementale du Québec has posted a guide describing several flow measurement methods on its web site (MDDEP 2008).

Environment Canada's hydrometric technician training manual is available on its web site. <u>http://www.ec.gc.ca/Publications/default.asp?lang=En&xml=DA898EF4-9F6C-486F-95DF-3D79109915C8</u> (last accessed November 28, 2011)

BC Environment has published a manual of standard operating procedures for hydrometric surveys in British Columbia (BC Environment 1998), which presents the criteria to be met to achieve various levels of precision. The manual also provides information on the standardized equipment used for taking measurements.

⁻ The U.S. government has an online technical guide describing various methods for the measurement of flow (USDI Bureau of Reclamation 2001).

⁻ The World Meteorological Organization has published a guide to hydrological practices that provides information on discharge monitoring and the measurement of precipitation (WMO 1994).

SYNTHESIS

MEASUREMENT INDICATORS FOR USE IN SMALL AGRICULTURAL WATERSHEDS ACCORDING TO PROBLEMS AND RESPONSE OBJECTIVES

In a context of limited resources, questions about the water quality monitoring strategy to be applied and its scope are inevitable. These questions may concern the type of indicators to be monitored, the number of measurement sites, the frequency and timing of the measurements and their duration (number of years), etc.

In Quebec, the issue of surplus phosphorus leading to accelerated eutrophication of waters is a major issue:

- if the objective of water quality monitoring is to identify affected bodies of water with a view to developing response priorities, the analysis of diatoms is a good option. The protocol used to monitor diatoms is fairly simple and inexpensive and involves limited sampling and few analyses. It can be tailored to a variety of water bodies; it does not entail flow measurements; and the results are easy to interpret.
- However, if the objective of monitoring is to detect specific causes of deterioration, physicochemical and bacteriological indicators must be selected. Depending on the indicators selected, the sampling strategy may require a more detailed sampling plan, minimal monitoring of rainfall, sampling during high flow periods, a larger number of samples and higher analytical costs.
- To analyze the impact of changes in watershed management practices, or to monitor the loads transported by a stream, a streamflow monitoring approach is required in addition to the preceding components. Monitoring of hydrologic indicators, depending on the desired level of precision, calls for more sophisticated and costly equipment, as well as technical expertise in order to analyze the results.

In agricultural landscapes, pesticide monitoring is an important issue, particularly in watersheds where pesticides are used intensively. Given the costs involved, pesticide monitoring requires specific strategies that must be developed in conjunction with specialists with the Department of the Environment.

For illustrative purposes, **tables 14 and 15** synthesize the main ideas presented in the previous sections concerning the development of appropriate strategies. **Table 14** presents the water quality monitoring protocols that are best suited to attaining the different objectives sought by proponents of monitoring projects. **Table 15** outlines a simplified approach to complement Table 14, and identifies the indicators to be measured depending on the water quality problems identified. Often, before monitoring objectives can be set, officials tasked with managing water bodies are made aware of perceived water quality problems.

Objective	Indicator	Sampling strategy and analysis	
Identify bodies of water affected by eutrophication	Diatoms	Simple, low cost. Initial diagnosis.	Sections 2.2.1 and 2.2.2
Verify the capacity to maintain uses Phosphorus, nitrates- nitrites, ammonia, fecal coliforms, suspended solids Rainfall, water level		Clearly define the uses to be protected Simple, more costly.	Section 1.2 and section 1.1.3 for index calculation
Determine the contribution of a watershed	Total phosphorus, Total nitrogen, Suspended solids Flow	More complex, requires precise monitoring of flow. Significant in terms of nonpoint source pollution	Section 1.2 for physicochemical parameters and sections 3.2.2 and 3.3.3 for discharge
implementation of beneficial management practices		Very complex. The more localized the management practices, the smaller the water quality changes to be detected, and the more difficult it is to detect a trend. High cost.	Only in introduction
Pesticide monitoring: Specific pesticides High cost; specific strategy.		High cost; specific strategy.	Not discussed

Table 14: Identification of objectives, selection of indicators, sampling strategy

Problem identified and impacts	Possible causes in the agricultural sector	Water quality parameters to be monitored
Erosion, presence of suspended solids Loss of uses, such as swimming, eutrophication, etc.	Drainage Denuded land Work done along shorelines	Suspended solids Turbidity Water level or flow Rainfall
Flooding of inhabited areas	Drainage Straightening of streams Loss of wetlands	Water level, flow Rainfall
Limitation of species' movements Loss of habitat, decline in biodiversity, loss of uses, such as fishing.	Silting of tributaries Culverts Impoundments	Presence and state of structures in streams Silting
Eutrophication — cyanobacteria Loss of uses: drinking water, water activities.	Nutrient loads: phosphorus and nitrogen Sediment loads	Diatoms Nitrogen and phosphorus concentrations Suspended solids Water level, rainfall
Presence of pathogens Loss of uses: drinking water, water activities, irrigation.	Animal waste on land that enters streams Livestock in streams	Fecal coliforms Water level, rainfall
Presence of pesticides Loss of uses: drinking water; irrigation, problem for aquatic life, contaminated fish tissue.	Crop spraying	Pesticides Water level, rainfall

Table 15: Identification of problems and selection of parameters to be measured*

* Adapted from COGESAF, 2006. Analyse du bassin versant de la rivière Saint-François. Partie 2: Diagnostic du bassin versant de la rivière Saint-François. p. 144. Table 6.1 "Liste des problèmes pouvant être rencontrés dans le bassin versant de la rivière Saint-François"

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ANNEX 1. GLOBO INDEX AND WATER QUALITY INDEX (WQI)

GLOBO Index (Sherbrooke)

The GLOBO index is a minimum operator index that was developed by Corporation de gestion CHARMES, an environmental protection and sustainable development firm in Sherbrooke, Quebec. It is an adaptation of the IQBP, using different parameters in the calculation. The index is based on the analysis of 11 parameters, including total nitrogen, pH, temperature, transparency, dissolved oxygen, and total organic carbon, parameters that are not used in the calculation of the IQBP. However, it does not include ammonia nitrogen or chlorophyll, two variables used in the calculation of the IQBP.

Like the IQBP, the GLOBO index analyzes water quality according to five classes; however, the water quality guidelines used for each quality class differ. The following table provides an example of the differences in the water quality guidelines used for Class A and Class D.

Table A. Indicators and threshold values used in the calculation of the IQBP and GLOBO indices

		reshold value defining high-quality water (Class A)		ning poor-quality water ass D)
	IQBP GLOBO		IQBP	GLOBO
Turbidity (NTU)	<=2.3	0.0 - 3.0	> 18.4	> 15
Suspended solids (mg/L)	<=6	<=3	>41	> 27
Fecal coliforms (cfu/100 i	mL) <=200	<=20	> 3,500	> 1,000
Ammonia nitrogen (mg-N	V/L) <=0.23	Not used	> 1.50	Not used
Nitrite-Nitrate (mg-N/L)	<=0.50	<=0.23	> 5.00	> 1.00
Total phosphorus (mg-P/	L) <=0.030	<=0.015	> 0.20	> 0.04

Source: Pers. comm., Corporation de gestion CHARMES. December 2009

Bulletin Eau, Corporation de gestion CHARMES. 2009 Bilan de la qualité des cours d'eau de Sherbrooke de 2005 à 2007.

The threshold values of the various quality classes were established on the basis of minimum and maximum values obtained for streams in the Sherbrooke region. According to the designers of GLOBO, the IQBP was not sufficiently discriminating to enable the identification of the most problematic sectors.

In general, the water quality guidelines used in the assessment of water quality are much more restrictive in the GLOBO index than in the IQBP. For example, the guidelines for fecal coliforms and phosphorus differ significantly between the GLOBO index and the IQBP. For water to be classified as being of good quality under the IQBP, the fecal coliform concentration must be less than 200 (cfu/100 mL), whereas under the GLOBO index, the concentration must be less than 20 (cfu/100 mL), for water to be classified as being of poor quality, the fecal coliform concentration must be over 3,500 (cfu/100 mL) under the IQBP and over 1,000 under the GLOBO index (**Table A**).

As we can see, there is a clear difference between the two indices. This appears to indicate that much more significant changes would have to be implemented to bring a watershed up to the good quality class under the GLOBO index than under the IQBP index. According to the designers of the GLOBO index, the more restrictive calculation values used in their index are justified in they allow stream degradation processes to be identified more rapidly, before they reach a critical level, and should also help to ensure a more rapid response to stream degradation problems. According to the designers of GLOBO, this index is better suited to the streams in the Sherbrooke area. It corresponds more specifically to water uses in the region (particularly swimming) (pers. comm., Corporation de gestion CHARMES, December 2009).

Water Quality Index (WQI)

The WQI was developed by the Canadian Council of Ministers of the Environment (CCME).

The way the WQI is calculated is described at the following web site: <u>http://ec.gc.ca/indicateur-indicators/default.asp?lang=Fr&n=0864F603-1&offset=4&toc=show#_ftn4</u> (Last accessed: April 5, 2011)

The WQI is calculated using the following formula:

$$WQI = 100 - \left[\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.72}\right]$$

Where:

F₁: Scope. Represents the percentage of the total number of parameters that fail to meet the water quality guidelines at any time during the reference period.

F₂: Frequency. Represents the percentage of individual tests that fail to meet the water quality guidelines.

F₃: Amplitude. Represents the average deviation of failed test values from their respective guidelines.

The WQI yields a number between 0 and 100 that is indicative of the overall water quality for a particular use. There are five classes: Excellent, Good, Fair, Marginal and Poor.

- Excellent (95.0 to 100.0): Water quality measurements never or very rarely exceed water quality guidelines.
- Good (80 to 94.9) Water quality measurements rarely exceed water quality guidelines and, usually, by a narrow margin.
- Fair (65 to 79.9) Water quality measurements sometimes exceed water quality guidelines and, possibly, by a wide margin.
- Fair (45 to 64.9) Water quality measurements often exceed water quality guidelines and/or exceed the guidelines by a considerable margin.
- Poor (0 to 44.9) Water quality measurements usually exceed water quality guidelines and/or exceed the guidelines by a considerable margin.

In 2005, MDDEFP conducted a comparative study of the IQBP and the WQI. The study underscored that the elements used in the calculation of the WQI differed from those used in the calculation of the IQBP. The study also showed that the IQBP, because it is a minimum-operator index, is generally more stringent than the WQI (Hébert 2005).

ANNEX 2. LIMITS OF STANDARD ANALYSIS METHODS

	Nitrates- Nitrites MA. 303 – NO3 1.1	Ammonia nitrogen MA. 303 – N 1.0	Fecal coliforms MA. 700 – Fec. Ec 1.0	Total nitrogen MA. 303 – Tot N 1.0	Total phosphorus MA. 303 – P 5.0	Suspended solids MA. 104 – S.S. 1.1
Interference	Metal ions in large concentrations, sulphides, chlorine, ferric ions and phosphates	Colour, turbidity and presence of suspended solids cause positive interference. Suspended solids and turbidity may be removed by filtration. Interference caused by colour may be eliminated by distillation.	Several sources of interference: see CEAEQ document	Interference can come from the colour of a sample that persists after digestion and can result in absorption of light in the region of the wavelength used. Sulphide concentrations of less than 10 mg/L cause variations of \pm 10% in nitrogen determination.	Arsenates and silica react with ammonium molybdate to form a blue complex. Hexavalent chromium and nitrites interfere at concentrations over 1.0 mg/L. Ferric ions, if present at over 100 mg/L, lead to the formation of a blue dye with ammonium molybdate. Since phosphorus is an abundant naturally occurring element and since this method is used for low concentrations, all contamination can lead to an overestimate of the phosphorus concentration. It is important that all samples also be acidified to avoid positive interference.	Highly mineralized water, whose content is hygroscopic, requires a prolonged drying time. Certain highly volatile solids may be lost during drying. For volatile suspended solids, the most significant interference is caused by organic matter unstable at 550°C.

	Nitrates- Nitrites MA. 303 – NO3 1.1	Ammonia nitrogen MA. 303 – N 1.0	Fecal coliforms MA. 700 – Fec. Ec 1.0	Total nitrogen MA. 303 – Tot N 1.0	Total phosphorus MA. 303 – P 5.0	Suspended solids MA. 104 – S.S. 1.1
Detection limit	0.02 mg/L NO3- NO2-N	0.02 mg/L NH3- N	1 CFU (colony forming units) by volume or filtered dilution	0.02 mg/L N	0.002 mg/L P	With 500 mL of water: 3 mg/L for filtrations with 1.2- µm filters and 5 mg/L for filtrations with 0.45-µm filters. With 1 L of water: 1 mg/L for filtrations with 1.2-µm filters.
Quantification limit	0.07 mg/L NO3- NO2-N	0.07 mg/L NH3- N	20 and 60 CFU of fecal coliforms	0.07 mg/L N	0.006 mg/L P	With 500 mL of water: 9.94 mg/L for 1.2-µm filters and 13.7 mg/L for 0.45- µm filters With 1 L of water: 3.5 mg/L for filtrations with 1.2- µm filters
Precision: Replicability	± 0.07 mg/L NO3-NO2-N at a concentration of 0.88 mg/L NO3-NO2-N (n=10)	± 0.01 mg/L NH3-N at a concentration of 0.19 mg/L NH3- N (n=10)	Not available	± 0.01 mg/L N at a concentration of 0.13 mg/L N (n=10)	0.003 mg/L P at a concentration of 0.273 mg/L P (n=10)	\pm 0.73 mg/L at a mean concentration of 29.9 mg/L with 1.2-µm filters and \pm 1.0 mg/L at a mean concentration of 24.1 mg/L with 0.45 µm filters (n=10)
Precision: Repeatability	= ± 0.04 mg/L NO3-NO2-N at a concentration of 0.81 mg/L NO3-NO2-N (n=10)	± 0.01 mg/L NH3-N at a concentration of 0.23 mg/L NH3- N (n=10)	The coefficient of variation (ratio of the standard deviation to the mean) was 16% at a mean concentration of 330 cfu/100 mL (n = 30).	± 0.11 mg/L NH3-N at a concentration of 0.74 mg/L N (n =10)	0.001 mg/L P at a concentration of 0.268 mg/L P (n=10)	± 1.5 mg/L at a mean concentration of 48.6 mg/L with 1.2-μm filters and ± 1.4 mg/L at an mean concentration of 19.5 mg/L with 0.45-μm filters (n=10)
Accuracy	95% at a concentration of 0.88 mg/L NO3- NO2-N (n=10)	97% at a concentration of 0.23 mg/L NH3- N (n=10)	The overall efficiency of the culture medium m-Fc, i.e., the proportion of typical and atypical colonies that were correctly identified, was 79%.	93%	96% at a concentration of 0.63 mg/L P (n=10)	93% for an expected concentration of 32.9 mg/L with 1.2- µm filters and 92% for an expected concentration of 26.1 mg/L with 0.45-µm filters (n=10)

Source: Méthodes d'analyses. Centre d'expertise en analyse environnementale du Québec (CEAEQ). http://www.ceaeq.gouv.qc.ca/methodes/chimie_inorg.htm. (last accessed May 11, 2010)

Sampling strategy

Sampling strategies designed to determine stream nutrient and sediment loads are more complex than monitoring programs designed simply to establish the state of contamination of a stream.

A number of studies conducted in Quebec indicate that the bulk of nonpoint source pollution occurs during spring floods. This means that monitoring from May to October, such as that established for *in situ* water quality monitoring as a function of various uses (IQBP calculation), does not make it possible to fully measure stream loadings, whether the pollutants/nutrients are deposited on site or are transported and deposited further downstream.

In agricultural watersheds, the three pollutants most commonly measured in water quality monitoring are phosphorus, total nitrogen and suspended solids. Since pollutant loads from nonpoint sources are primarily affected by rainfall, the monitoring of loads must necessarily capture a certain number of rainfall events. The sampling period should therefore include, at a minimum, the snowmelt period, intense summer rainfall events and autumn rains before the first frost. Where possible, monitoring should also be conducted in winter.

Calculating pollutant and nutrient loads requires not only knowing the concentration of the parameter monitored, but also the corresponding volume of water. This means that load monitoring requires that streamflow be monitored as precisely as possible, as described above. The sampling station must be located at the mouth of the stream draining the watershed under study. The first step is therefore to carefully define the boundaries of the watershed and clearly identify the main stream that drains the entire watershed. If the objective is to measure loads from a particular area (on a portion of watershed or several watersheds, such as, for example, a farmer's fields), the watershed or watersheds that drain the area must be identified, along with the points where streams enter and exit the watershed. To be precise, it is essential to conduct complete monitoring at the inlet and outlet (upstream-downstream type).

Samples must be taken during all four seasons of the year to ensure than they are representative of various stream discharge levels (high flows, "average" flows and low flows) and different states of vegetation cover and land use in the watershed. It is also very important to clearly note the height of the water on the staff gauge and the time of sample collection, particularly during high flow events. The concentration of the parameters is not necessarily the same during rising waters than during receding waters; it is therefore useful, when calculating pollutant/nutrient loadings, to know at what point in the high flow event the sampling was conducted. It is also necessary, where possible, to collect samples as flood waters are rising and as they are receding.

The number of samples collected is generally limited due to budgetary reasons. It is therefore important to reconcile the need to maintain an affordable cost with the need to obtain the best possible representation of reality.

If load monitoring is conducted at the same time as *in situ* water quality monitoring, samples can be collected from May to October on a regular basis, adding samples collected during rainfall events specific to each season.

Sample collection

(See section 1.2.2)

Sample analysis methods

In the calculation of loadings, phosphorus, nitrogen and suspended solids must be analyzed using standard methods. Simplified methods cannot be used to monitor loads because their margin of error is too large, particularly if the objective is to establish comparisons between various watersheds.

(See section 1.2.3)

Presentation, analysis and interpretation of results

Besides the general rules governing the presentation of results (see section 1.2.4), there are a few additional requirements that apply to the analysis and interpretation of the load results.

The first step in the calculation of load involves determining what is known as flux. For example, the phosphorus flux in a stream at a given time is calculated as follows:

$$F_{phosphoru}\left(\frac{mg}{hour}\right) = C_{phosphoru}^{o}\left(\frac{mg}{L}\right) \times Q\left(\frac{L}{hour}\right)$$

F	:	Phosphorus flux in milligrams per hour
C	:	Phosphorus concentration at a given time in milligrams per litre
Q	:	Streamflow at a given time in litres per hour

If the water sampling time step is relatively small, the phosphorus load transported by the stream over a longer period of time (day, month, year) can be calculated on the basis of the phosphorus flux.

In order to calculate load over a given period, the conditions must remain constant during that period (phosphorus concentration and streamflow). Over a period of one day, if it does not rain, the conditions may be stable, but to establish the load over a longer period, it is essential to take variations in streamflow and concentration over time into account. The calculation of flux is only possible if instruments are installed for advanced monitoring (see section 3.3).

Because probes are now available at an affordable cost, allowing the continuous measurement of water levels (the interval between the measurements can be a few minutes), temporal variations in streamflow can be measured easily.

However, tools for continuous measurement of concentrations do not exist for all parameters (e.g., phosphorus) and those that do exist are generally costly.

Also, generally speaking, if continuous water level monitoring is possible, concentrations are generally measured in grab samples. To establish the load transported by a stream over a period of one year using grab sample concentration data, a formula that defines the flow vs. concentration relationship, providing the best representation of reality (with the smallest possible error), must be used.

There is a large number of different equations (Birgand 2009; Smart et al. 1999) that can be used to plot concentration-flow relationship graphs. However, the U.S. Army Corps of Engineers has developed software that proposes six different methods for calculating annual loads of phosphorus or other pollutants transported by a stream. The software allows the user to choose the most representative method. This software is used by a large number of water quality monitoring specialists in the United States and Quebec. A Windows version (beta) of this software named FLUX is available free of charge online (U.S. Army Corps of Engineers 2004).